THE THERMODYNAMIC ACTIVITY OF CARBON IN LIQUID IRON

- AN EXPERIMENTAL INVESTIGATION -

THESIS

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by

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CHAPTER I

INTRODUCTION

INTRODUCTION

At present unprecedented advances are being made in science and technology. It is probably true to say that the majority of these scientific advances, however, would not have been possible except for developments in the iron and steel industry since today little or no industrial progress is possible without the use of iron or steel whether directly, or indirectly in the manufacture of other products.

The development of iron production dates back in this country to the Roman Period (2nd Century A.D.) when the earliest known shaft furnace was used to produce iron. This development has proceeded through the centuries resulting in the modern iron blast furnace which is still the main producer of iron and is likely to remain so in

the/

the forseeable future.

The development of the blast furnace has been an art rather than a science but recently the necessity for the scientific approach has been appreciated. Thus, during the last half century a great deal of work and thought has been devoted to the increase of blast furnace efficiency. The practical ironmaker, however, is chiefly interested in the quantity rather than the quality of the iron with the result that sintering, pelletizing, increased blast temperature, oxygen enrichment of the blast, coal and oil injection, water vapour additions to the blast, high top pressures, improved refractories etc., have all been tried in an attempt to achieve maximum iron output while keeping the coke rate as low as possible. This approach, although essential, does not improve the quality of the iron and this /

this must also be considered since an improvement of the iron quality will reduce the work required in the steelmaking furnace. Also, at present, with the increasing use of the Pneumatic Steelmaking Process it is important that consistent iron quality should be obtained from the blast furnace.

In order to predict the optimum quality of iron obtainable for certain given materials, it is necessary to study the refining reactions occurring and the theoretical equilibria which may be attained within the blast furnace.

The two elements which have been most widely studied with regard to blast furnace practice are sulphur and silicon, in an attempt to keep those elements as low as possible in the resultant iron. The most exact information available, however, is for the sulphur reaction which may

be /

be expressed as follows:-

$$[FeS] + (CaO) = (CaS) + (FeO) \quad .....(1)$$

$$C + (FeO) = Fe + CO \quad .....(2)$$

The Overall reaction being:-

$$[FeS] + (CaO) + C = (CaS) + Fe + CO \quad .....(3)$$

It has been found that this reaction does not reach equilibrium which may be due to the slag-metal reaction (1) or the slag (metal)- carbon reaction (2) or both of them not reaching equilibrium. If the oxygen potential of the system relative to pure graphite could be measured then the extent to which reaction (2) had approached equilibrium could be measured and hence the approach of reaction (1) to equilibrium would be known. Thus it is desirable to measure the oxygen potential of the slag in equilibrium with pure graphite.

It might be thought that the easiest method of

measuring /

measuring the oxygen potential of the slag would be to measure its FeO content. This, however, is a very difficult analytical problem due to the presence in the slag of finely divided iron which cannot be satisfactorily separated from the slag by magnetic means. For this reason the measurement of the oxygen potential of the system by means of FeO determination is practically impossible by present techniques. The oxygen potential must, therefore, be studied by some other method.

An apparently promising reaction is that involving manganese

$$MnO = Mn + 1/2\ O_2$$

since this also gives a measure of the oxygen potential of the system. In this case the analysis is more straightforward and reliable. There is, however, a very pronounced temperature /

temperature coefficient for the above reaction and hence it is essential to have an accurate temperature measurement. Unfortunately this is exceedingly difficult to obtain. There is also a lack of knowledge of the activity of MnO in the slag solution and of the activity of manganese in iron-carbon alloys. Thus, at present, there is little useful information to be gained by this approach.

It has been shown that iron from the blast furnace is unsaturated with respect to carbon. A value of approximately 0.6 for ΔC (the difference between the observed carbon content and the saturation solubility of carbon, allowing for the effect of the metalloids present) has been obtained [1] from a study of data on operating furnaces. If it is assumed that the carbon in the iron is in equilibrium with the oxygen in the iron and hence in the slag, then the carbon /

carbon activity of the iron can be used to assess the oxygen potential of the system relative to pure graphite as follows:-

$$C\ (gr.) + 1/2\ O_2 = CO$$

$$p\ O_2^{\frac{1}{2}} \propto \frac{pCO}{1} \qquad \text{since } a_c = 1$$

The observed value

$$p'\ O_2^{\frac{1}{2}} \propto \frac{pCO}{a_c}$$

p' is the oxygen potential when the system is not saturated with carbon.

$$\therefore \quad \frac{p'\ O_2}{p\ O_2} = \frac{1}{a_c^{\,2}}$$

Thus it can be seen that a solution of the above problem would be obtained if data on carbon activity in iron were available at medium to high carbon concentrations.

For this reason, as well as a desire to widen the general thermodynamic data, it was decided in the present work to study the activity of carbon in the range 1 - 5% carbon /

carbon since although much research has been performed on alloys containing 1% carbon in iron the data at higher concentrations is extremely sparse and inconsistent. Consequently, predictions of behaviour up to carbon saturation have been based on rather dubious assumptions. A thorough examination of the iron-carbon binary is also an essential step prior to studying ternary systems in an attempt to find interaction coefficients between the elements concerned.

CHAPTER II

LITERATURE SURVEY

LITERATURE SURVEY

From what has been written in the introduction the need for research on the activity of carbon in iron can be appreciated. This need has been acknowledged for a number of years and much work has been carried out in this field.

The first indication that carbon in iron did not form an ideal solution was obtained by studies of the solubility product ($\underline{m} = \%C \times \%O$). From these studies (2) it was found that m was not constant, as it would be if both carbon and oxygen behaved ideally, but did in fact increase with carbon content. Thus in the reaction

$$\underline{C} + \underline{O} = CO$$

where K' is the equilibrium constant and

$$K' = \frac{pCO}{m}$$

pCO is the partial pressure of carbon monoxide

$\underline{C}$ and $\underline{O}$ represent percentages of carbon and oxygen in iron solution.

the value of K' was found to decrease with increasing carbon content. Since it had been shown that oxygen obeys Henry's Law the decrease in the value of K' with increasing carbon content must be attributed to the fact that carbon does not obey Henry's Law and consequently activity values must be substituted for the weight percentages.

In order to obtain activity measurements detailed research into the iron-carbon binary system was necessary. This work has been carried out both experimentally and theoretically by thermodynamic calculations, such calculations normally being based on assumptions which can only be verified by suitable experimental evidence. In this survey it is proposed to review first the experimental work /

work and then the theoretical contributions for the determination of carbon activity based on thermodynamic calculations.

Experimental Techniques for the Determination of a_C

Several well established techniques are available for activity measurements. Some of these are applicable to the determination of the activity of carbon in iron, for example gas metal reactions, E.M.F. measurements, or vapour pressure measurements of iron in an iron-carbon melt and hence by a Gibbs-Duhem integration the determination of carbon activity. Experimental studies carried out to date using some of these techniques are discussed below.

Gas - Metal Reactions

Two /

Two gas metal reactions which can be used to find the activity of carbon in iron are

$$\underline{C} + CO_2 = 2CO \quad \ldots\ldots (1)$$

$$\underline{C} + 2H_2 = CH_4 \quad \ldots\ldots (2)$$

Work has been carried out using both of these reactions and the literature survey is divided into a section dealing with the carbon monoxide - carbon dioxide reaction and a separate section on the hydrogen - methane reaction.

Experimental studies of carbon in liquid iron using the carbon monoxide - carbon dioxide reaction

Marshall and Chipman [2] carried out a most comprehensive if not very exact study of the carbon - oxygen equilibrium in molten iron. The equilibria involving the activity of carbon was

$$\underline{C} + CO_2 = 2CO$$

The /

The equilibrium constant for the reaction

$$K' = \frac{pCO^2}{pCO_2 \times a_c} = \frac{r_1}{a_c}$$

where a_c represents the carbon activity and the gas ratio $r_1 = \frac{pCO^2}{pCO_2}$, pCO and pCO_2 being the partial pressures of the respective gases.

Marshall and Chipman's (2) experimental runs were carried out in a furnace especially designed to work up to twenty atmospheres pressure in order to study the solubility product while at the same time being able to carry out activity measurements. The melt, contained in a magnesia crucible, was brought to temperature (varying temperatures up to 1540°C were used) in a reaction chamber, filled with a carbon monoxide - carbon dioxide mixture and the system was left to attain equilibrium between the melt and the gas mixture. When equilibrium was reached /

reached a gas sample was drawn off and analysed, the melt was quenched and the amounts of carbon and oxygen in the melt was determined. By this technique results were obtained up to 2.4 per cent carbon. By plotting the gas ratio against the weight per cent a linear relationship was obtained up to 0.5 per cent carbon, thus below this value the activity of carbon is equal to the weight per cent when 1% infinite dilution scale is taken as the standard state.

Hence $K_1' = \frac{r_1}{\%C} = K_1$ at low concentrations.

From the curve of r_1 against %C, Marshall and Chipman [2] obtained a value of $K_1 = 430$. Thus at any concentration

$$f_c = \frac{a_c}{\%C} \quad \therefore \quad K_1 = \frac{p^{2CO}}{pCO_2 \times (f_c \times \%C)}$$

$$\therefore \quad f_c = \frac{K_1'}{430}$$

Thus f_c can be calculated and hence a_c.

Later /

Later work [3, 5-7] showed the results of Marshall and Chipman [2] to be rather inaccurate and the value of 0.5 per cent carbon for the limit at which Henry's Law holds appears to be high. The following sources of error may have been significant in their work.

a) Thermal segregation of the gas atmosphere, although an attempt was made to overcome this by inserting a small fan in the reaction chamber.

b) Reduction of the magnesia crucible by the carbon in the iron, producing carbon monoxide.

c) Carbon deposition from the gases during sampling $2CO = C + CO_2$ resulting in an inaccurate gas analysis.

Although, the results of Marshall and Chipman [2] do not now appear reliable in view of these possible sources of /

of error and also subsequent results, the technique which they used involving the carbon monoxide - carbon dioxide reaction is substantially the same as that employed in other subsequent studies.

Dennis and Richardson [3] whose data at higher temperatures (1560°, 1660° and 1760°C) appears to be the most reliable to date, held a bead of the iron-carbon alloy in a lime, magnesia or alumina boat. Carbon monoxide - carbon dioxide mixtures were passed over the bead of metal until equilibrium had been attained, the metal then being quenched and analysed for carbons. The highest carbon content at which work was undertaken was 1.08 per cent carbon, this being attained with a gas ratio of 820 at 1560°C. Accurate work at higher gas ratios was prevented by the experimental difficulties associated with /

with metering very minute quantities of carbon dioxide, since the equilibrium gas ratio increases very rapidly with increasing carbon content of the melt. This difficulty combined with that of the carbon deposition reaction appears to have been the limiting factor in all experimental studies of this type and virtually precludes the use of this technique at relatively high carbon contents.

The results obtained by Dennis and Richardson [3] with lime and alumina boats showed good agreement but it was found that the errors with a magnesia boat were considerable at 1660° and 1760°C. The error is because magnesium has a higher vapour pressure than calcium or aluminium and hence due to the loss of magnesium into the gas phase the following reaction can occur :-

$$MgO + \underline{C} = CO + \underline{Mg}$$

The /

The carbon monoxide thus formed would alter the gas ratio which would account for the error with the magnesia crucible. A similar reaction will occur to a lesser extent with lime and alumina crucibles but the extent to which it will interfere is dependent on the kinetics of the reaction and this can only be determined by experiment.

The activity of carbon was calculated using known free energy data for the reaction : $C\ (gr) + CO_2 = 2CO$ thus enabling the equilibrium constant to be determined, using graphite saturation as the standard state. It was found that the activity was not markedly temperature dependent but the deviation from Henry's Law was marked above about 0.2 per cent even at 1760°C.

Rist and Chipman (4) tried to extend the work of

Dennis /

Dennis and Richardson [3] to higher carbon contents by a similar technique with suitable modifications in an attempt to control the gas ratios. In order to achieve a better control of the gas mixture, argon was added thus giving an increase total flow rate and subsequent benefits in control of the gas composition. Gas ratios up to 1150 at 1560°C, were passed over the melt until equilibrium was attained and the melt was cooled in an argon atmosphere. The maximum carbon content at which runs were performed was 1.29 per cent at 1560°C, much of the work being performed at this temperature, and 4.38 per cent carbon at 1360°C. Results were also obtained at 1260°C.

The results are limited in this study to three equilibrium points at 156o° and one at 1460°C. At 1360° and 1260°C no reliable data was determined. The limited

scope /

scope of the results appears to be due to one or all of the following reasons, (a) carbon deposition (b) thermal diffusion and (c) lack of thermal equilibrium between the gas and the hot metal.

Banya and Matoba [5] have performed the most recent work by use of the carbon monoxide - carbon dioxide mixture with gas ratios from 45 to 3120. In order to achieve these very high ratios very careful control of the gas composition and flow rates were necessary. Runs were carried out at 1460, 1560, 1660 and 1760°C, a particularly large number being performed at 1560°C with carbon contents up to 2.02 per cent carbon. From the experimental results Banya and Matoba [5] plotted

$$\log K_1' \left(= \frac{pCO^2}{pCO_2 \, N_c} \right) \text{ against } N_c$$

This /

This, was found to give a straight line up to 0.09 N_C

Since $\log K_1' = \log K_1 + \log \gamma_C$

where γ_C = activity coefficient of carbon

and K_1 is the equilibrium constant for a Henry's Law standard state.

The value of the equilibrium constant (K_1) can be obtained from the equation of the graph, and hence the activity of carbon can be calculated. The results obtained will be discussed at a later stage.

Experimental Study of Carbon in Liquid iron using the hydrogen - methane equilibrium

As stated above another possible gas-metal equilibrium which can be used to measure carbon activities is the reaction $\underline{C} + H_2 = CH_4$ . . . . . (2)

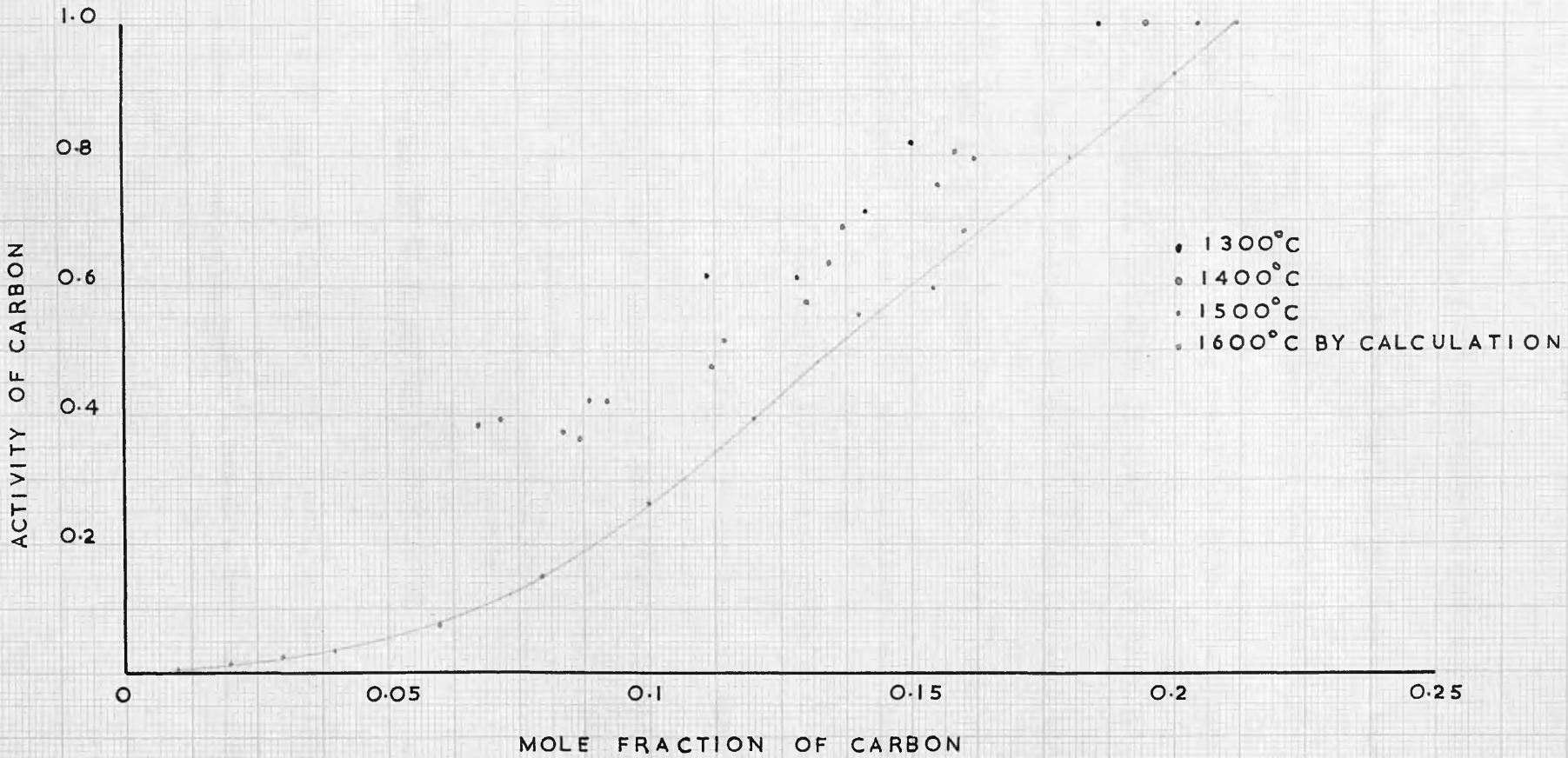
Turkdogan, Leake and Masson [6] equilibrated hydrogen with iron-carbon melts. The experiments were carried out in a closed /

closed system where hydrogen was circulated over an iron-carbon alloy held in a lime crucible. Connected to the system was an infra-red gas analyser adapted to measure the amount of methane formed. When the methane reached a steady value it was assumed that equilibrium had been attained and the melt was quenched and analysed for carbon. An alumina tube was used as the reaction chamber and a cold trap containing solid carbon dioxide was inserted in the system. The reason given for the inclusion of the cold trap was that calculations based on available thermodynamic data indicated that if the water vapour pressure in the system was that of ice at liquid oxygen temperature about 10^{-20} atm. of methane would be sufficient to form aluminium carbide from alumina at high temperatures. On the other hand if the partial pressure of water vapour in the reaction chamber was adjusted /

adjusted to that of ice at 0°C oxidation of methane would occur.

Experiments were carried out at three temperatures 1300, 1400 and 1500°C, but at 1500°C there were very few results (only three values being given). This was stated to be due to alumina tubes developing pin holes, after a day or two of continuous use, which resulted in the oxidation of the methane. Also at higher temperatures and at low carbon concentrations it was very difficult to measure the methane formed by the gas analyser since the ratio $\frac{pCH_4}{pH_2^2}$ becomes smaller with decrease in carbon concentration and increase in temperature.

Carbon activities derived up to 3.99 per cent carbon using available equilibrium data for the free energy of formation of methane [7]. This data was also used to check /



GRAPH I RESULTS OF TURKDOGAN, LEAKE AND MASSON FOR THE ACTIVITY OF CARBON

check the reliability of the experimental procedure by measuring the hydrogen/methane ratio in equilibrium with graphite and very good agreement was found between the experimental results and the available data. Turkdogan et al's [6] results are shown in Graph 1 from which it is apparent that the activity values show considerable scatter. At 1300 and 1400°C the results give some indication of the activity at higher carbon concentrations than those obtained by any of the carbon monoxide - carbon dioxide equilibrium studies, but at 1500°C it can be seen that the reproducibility is extremely poor and little reliable information can be deduced.

Experimental Study of carbon in solid iron

It is relevant to refer also to work on the activity of carbon in austenite, since these data have been used as /

as a basis for the prediction of activities in the liquid state.

In a paper presented in 1946 Smith [8] obtained activity values for carbon in solid iron by use of both the hydrogen - methane and the carbon dioxide - carbon monoxide reactions.

The iron sample was in the form of a strip (about 0.2mm thick, 1cm wide and 6-15 cm long) wound into a coil and suspended from a platinum wire, in the reaction chamber. An upstream flow of the given gas mixture was passed over the coil at a fixed temperature until equilibrium was attained. The specimen was then quenched and analysed for carbon. The range of compositions covered was from 0.008 per cent to 1.5 per cent carbon in solid iron.

With /

With hydrogen - methane mixtures runs were carried out at 750, 800 and 1000°C with 0 - 5 per cent methane in the mixture, but attempts which were made to carry out the experiment at 1200°C were unsuccessful due to silicon pick up from the porcelain tube.

Runs were carried out at 800, 1000 and a few at 1200°C employing the carbon monoxide - carbon dioxide equilibrium, with 0.3 - 27 per cent carbon monoxide in the mixture. The equilibrium constants for the carbon monoxide - carbon dioxide and the hydrogen - methane reactions were determined directly at 800 and 1000°C as follows. Different gas ratios were passed over a block of "Acheson" graphite (impregnated with a small amount of iron to act as a catalyst) and the gain or loss in weight of the block was measured. The gas ratio corresponding

to /

to a constant weight of the graphite block was taken as being equivalent to the equilibrium constant.

The equilibrium constant was also measured indirectly by extrapolating the gas ratio for various percentages of carbon content up to the composition where austenite is in equilibrium with graphite and hence the activity of carbon is unity. The gas ratio then corresponds to the equilibrium constant.

The values of the equilibrium constants showed reasonable mutual agreement when measured directly and indirectly, but did not correspond to the available thermodynamic data [9]. Smith [8] based all his calculations on his own values for the equilibrium constant, ignoring the other data, on the assumption that any errors in his values for the equilibrium constants would /

would be similar to those in his activity measurements, since the same procedure was used and hence any errors would be self cancelling. Whether this assumption is justified or not is a debatable point.

It was also found that the activity of carbon from the hydrogen - methane equilibrium was slightly different from the value obtained with the carbon monoxide - carbon dioxide equilibrium. This may be due to impurities such as oxygen, hydrogen or silicon in the metal resulting from the experimental technique used.

A very similar technique to that employed by Smith [8] was used by Schenck and Kaiser [10] to determine the activity of carbon in austenite at 800 and 1000°C. In this study the hydrogen - methane equilibrium was employed with 0 - 1 per cent methane in the mixture. The gas was circulated /

circulated over the metal sample until equilibrium was attained, the methane being measured by means of an infra-red gas analyser.

The equilibrium constant for the hydrogen - methane reaction was determined at 800, 850, 900, 950 and 1000°C and the values obtained were in excellent agreement with those of Smith [8] at 800 and 1000°C. This study confirms the results of Smith [8] for the activity of carbon in γ-iron, the results agreeing well with Smith's [8] plot of carbon activity against percentage carbon in iron.

The manner in which Smith's [8] results have been used to derive values for a_c in the liquid state will be discussed subsequently.

Experimental Study of carbon in liquid iron by use of E.M.F. measurements

Sanbongi /

Sanbongi and Ohtani [11] measured the activity of carbon in liquid iron at 1450, 1500 and 1550°C by means of electromotive force measurements in an electrochemical cell of the type :-

Liquid iron-carbon alloy / Carbide Slag / Liquid iron-carbon alloy (saturated with carbon).

The cell consists of two silica U-tubes which are connected by a small limb. Carbon saturated iron is placed in one of the U-tubes and covered with powdered graphite while the alloy of unknown carbon activity is placed in the other U-tube. A carbide slag acting as an electrolyte is then packed on top of the metal and across the junction between the two tubes thus completing the concentration cell. The cell is heated in a graphite crucible by means of induction heating and the potential difference between the two arms of the cell is measured by dipping graphite electrodes /

electrodes into the melts. The activity of carbon was then calculated from the following expression:

$$E = - \frac{0.0002}{n} T \log a_c$$

Where E is the electromotive force

n is the ion valency

and T is the temperature

n was found to have a value of 2 approximately and hence the activity could be calculated.

By this technique activity measurements were made up to 4.39 per cent carbon at 1550°C and the results indicated that Henry's Law was obeyed up to 0.8 per cent carbon. In this respect the results differ from most of the other measurements made. Although the results are rather scattered and show some inconsistency, this technique would appear to have the advantage of simplicity. It is theoretically attractive but considerable experimental difficulties /

difficulties have been found to arise in other studies of this type. Particular care must be taken to avoid side reactions and to obtain an accurate value of n for the cell.

The above summary includes the most important of the experimental studies on the measurement of carbon activity in the iron - carbon binary system which have been reported to date.

Thermodynamic Calculations for the Determination of Carbon Activity

As can be seen from the previous section of the literature survey, most of the experimental work carried out deals with iron carbon alloys up to 1 per cent carbon, with a few scattered experimental results up to 4 per cent carbon. In order to obtain some indication of the activity /

activity of carbon at high concentrations in liquid iron, it has been found necessary to resort to thermodynamic calculations based on certain assumptions to allow extrapolation of the experimental results at lower carbon concentrations. Whether the assumptions made are valid for the iron - carbon system is hypothetical and the validity can only be proved or disproved by experimental evidence.

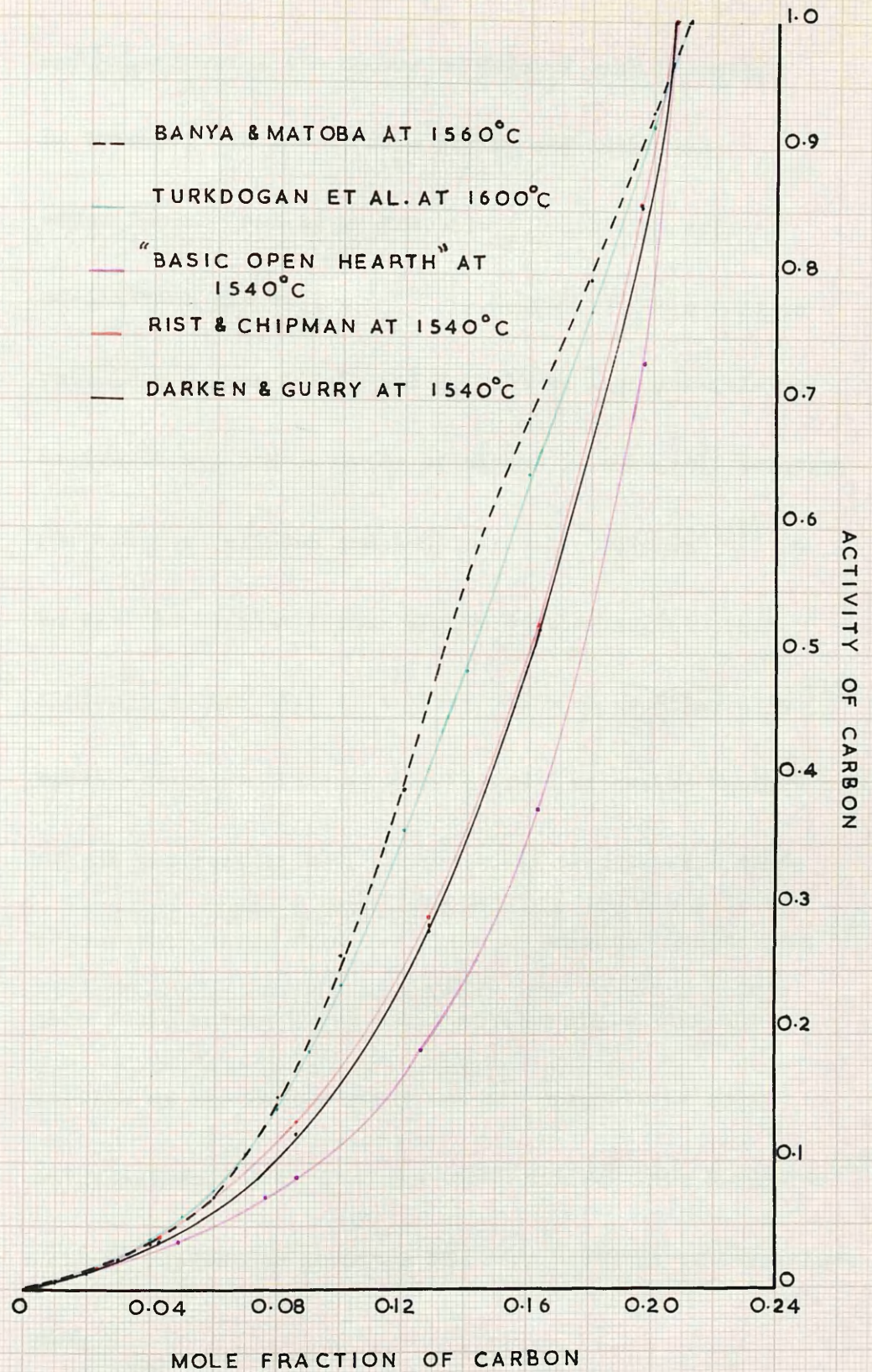
Darken [12] assumed that in iron - carbon melts the molecular species present are Fe, C and Fe_3C. Regarding the solution as ideal and taking the activity of graphite as unity the following relationships can be deduced :-

$$C\ (\text{graphite}) = \underline{C} \qquad K_1 = \frac{[\underline{C}]}{N}$$

$$C\ (\text{graphite}) + \underline{3Fe} = \underline{Fe_3C} \qquad K_2 = \frac{[\underline{Fe_3C}]\ N^2}{[Fe]^3}$$

Where N = total no. of mols = $[Fe] + [Fe_3C] + [C]$

and /



GRAPH II COMPARISON OF VALUES OBTAINED FOR THE ACTIVITY OF CARBON IN IRON

and [ ] represents the number of mols of each species. By assuming the law of mass action and using the experimental results on graphite solubilities and equilibrium gas ratios [13-16], Darken [11] was able to calculate values for K_1 and K_2. It is then possible to derive values for activity of carbon in the metal solution for all compositions and temperatures. Chipman [17] in an article in "Basic Open Hearth Steelmaking" appears, although no indication is given, to have used Darken's [12] results to plot activity coefficients of carbon against weight per cent carbon. Since these results were taken rather than those from the study by Marshall and Chipman [2] this would substantiate the statement above that the results of the latter study are not regarded as being satisfactory. A plot of the curve derived from Darken's [12] work is reproduced in Graph 11. For the sake of comparison with /

with other work this curve has been recalculated on to a Raoult's Law basis and it can be seen from the graph that Henry's Law only holds up to 0.2 per cent carbon.

The validity of this curve is extremely doubtful since numerous assumptions are involved in its calculation, namely the molecular species present in the solution and the ideal behaviour of the components. The data on which K_1 and K_2 are calculated is also suspect and there is a further assumption on the temperature dependence of K_1 and K_2.

Another approach was made by Darken and Gurry [18] who assume that carbon in a liquid iron - carbon alloy has a constant α function (where $\alpha_i \equiv \frac{\ln \gamma_i}{(1 - N_i)^2}$, γ_i being the activity coefficient of the species i, and $\gamma_i = \frac{a_i}{N_i}$) from zero carbon content up to saturation.

Hence /

Hence $\log \gamma_{c^1} = \alpha (N_{Fe}^{1})^2$ (the superscript 1 denoting the liquid phase).

It is then assumed by Darken and Gurry [18] that the α function for the other component iron is also constant in the solution, hence :-

$$\log \gamma_{Fe^1} = \alpha (N_c^{1})^2$$

To determine the value of α at various temperatures, Darken and Gurry [18] used the results of Smith [8] on carbon activity in austenite, together with solubility data and vapour pressure measurements from other sources [13,19-21].

The relationship $\ln a_{Fe}^{\gamma} = - \frac{N_c^{\gamma}}{N_{Fe}^{\gamma}} - 3.3 \left(\frac{N_c^{\gamma}}{N_{Fe}^{\gamma}} \right)^2$ (where the superscript γ indicates in austenite), derived from Smith's [8] results, was assumed to hold for iron in austenite at all temperatures. The activity of iron in austenite could then be determined at the austenite - liquid phase boundary and combined with the data for the free /

free energy of fusion of γ-iron it was possible to find the activity of iron in the liquid phase. By this calculation the α function was found for the Graphite Eutectic (1153°C) and at the δ-γ-Liquid Equilibrium (1492°C). The α function was also obtained in the vicinity of 1600°C [20] and from vapour pressure measurements at 2650°C [21]. These results were then plotted on a graph of α function against 1/T (where T is the absolute temperature) and although the points were somewhat scattered they approximated to a straight line through the origin.

By representing the α function by A/T (where A is a constant, the slope of the line) the following relationship was obtained from the graph,

$$\log \gamma Fe^{1} = -\frac{4660}{T} (N_c^{1})^2$$

The /

The standard state being $\gamma_{Fe}^{1} = 1$ when $N_{Fe}^{1} = 1$.

In order to determine a reciprocal equation for the activity coefficient of carbon, Darken and Gurry (18) changed the standard state since a reciprocal standard state for carbon would be unrealistic. By choosing graphite saturation as the standard state for carbon ($a_c^1 = N_c^1 . \gamma_c^1 = 1$) at any particular temperature then

$$\log \gamma_e^1 = -\frac{4660}{T}\left[(N_{Fe}^1)^2 - (N_{Fe}^{1\ sat})^2\right] - \log N_c^{1\ sat}$$

where the superscript sat indicates a saturated solution. From this equation a plot of activity of carbon against mole fraction was drawn and it is also shown in Graph II.

The validity of this graph is extremely dubious for the following reasons. Very few metallic solutions have a constant α function and there is no reason why this assumption should be correct in the iron - carbon system/

system. However if a constant α function is assumed it limits the need for other assumptions which may or may not be justified. However, Darken and Gurry [18] proceed to make a further assumption, that the α function is proportional to 1/T. This actually implies, though the fact is not stated, that carbon forms a regular solution in iron, which, to say the least, is extremely unlikely.

A very similar calculation was performed by Rist and Chipman [4] using their own very limited experimental results together with those of Dennis and Richardson [3]. Rist and Chipman [4] plotted the function $\log K_1''$ (where $K_1'' = \frac{p^2CO}{pCO_2\ N_c}$) against $(1 - N_{Fe}^2)$ at different temperatures. Since most of the experimental data related to a temperature of 1560°C this isotherm was drawn as a straight line through the experimental points /

points to the point of graphite saturation. This assumes that log K_1'' is proportional to $(1 - N_{Fe}^2)$ which in effect assumes a constant α function. Linear isotherms for the other temperatures were drawn on the assumption that their slopes were proportional to 1/T and hence could be calculated from the slope of the 1560°C isotherm. Since log K_1'' is related to log γ_c by the expression log $K_1'' = \log K_1 + \log \gamma_c$, it allows a relationship of the form $\log \gamma_c = -\frac{A}{T}(1 - N_{Fe}^2)$ to be obtained. As pointed out above in connection with Darken and Gurry [18] this expression in effect assumes a regular solution although this is not pointed out by either Darken and Gurry [18] or by Rist and Chipman [4]. However, since an equation of this type did not give agreement with the points corresponding to graphite saturation at all temperatures /

temperature, it was necessary to introduce an empirical temperature coefficient for A and the following expression was given, representing the best fit with the experimental data:

$$\log \gamma_c = \frac{4350}{T}\left[1 + 4 \times 10^{-4} \quad (T - 1770)\right] 1 - N_{Fe}^{2}$$

A plot of activity of carbon from this expression at 1540°C against mole fraction is shown in Graph 11.

From this graph a very close relationship can be seen between the results of Rist and Chipman [4] and Darken and Gurry [18] which at first sight may appear to be support for the validity of their calculations. The agreement is not so surprising however when it is considered that almost identical assumptions have been used to predict the temperature and composition dependence of the activity, namely that there is a

constant /

constant α function and that behaviour is that of a regular solution in the case of Darken and Gurry [18]. This latter assumption is slightly modified by Rist and Chipman [4] assuming an empirical correction to the constant A. It can be seen therefore that experimental results at higher carbon levels are required to show whether these rather sweeping assumptions are valid.

Turkdogan et al [6] as has been mentioned obtained some results up to 3.99 per cent carbon at 1500°C. In an attempt to obtain results over the whole range of compositions Turkdogan et al [6] plotted a graph of $\frac{\log a_C N_{Fe}}{N_C}$ against $\frac{N_C}{N_{Fe}}$ and found the former function to be approximately constant from 0.14 N_C up to saturation. From this graph the relative partial molal heat of carbon ($\overline{\Delta H_C}$) was found to be 3,200 ± 1300 cal/mole for 0.14 N_C up to saturation whereas Dennis and

Richardson /

Richardson [3] had obtained a value in dilute solutions i.e. $N_c < 0.025$ of $\overline{\Delta H}_c = 6,400 \pm 2000$ cal/mole. Turkdogan et al [6] pointed out that a value of 4400 cal/mole could be obtained within the error limits of the two sets of results. This value of $\overline{\Delta H}_c$ was then assumed to be independent of temperature and composition within the limits of accuracy of the results and hence $\overline{\Delta S}_c$, the partial molal entropy of solution of carbon was calculated. From these values, the activity of carbon could be calculated at any temperature or composition. The results of this calculation at 1600°C are shown in Graph 11.

The assumption that $\overline{\Delta H}_c$ is independent of composition results in the heat of mixing curve being linear which is extremely unlikely. This is also directly opposed

to /

to Darken and Gurry's [18] calculations which assume a regular solution and hence a parabolic heat of mixing curve.

Banya and Matoba [5] performed a similar calculation by assuming $\overline{\Delta H}_C$ independent of composition, to extend their results from 2.02 per cent carbon, at 1560°C, up to saturation. A graph of log γ_C against N_C was plotted and it was shown that up to 0.09 N_C a linear relationship was obtained. A value of $\overline{\Delta H}_C$ of 4130 ± 1000 cal/mole was calculated up to 0.09 N_C and it was assumed to be independent of composition over the whole range of concentration of iron-carbon alloys. Hence $\overline{\Delta S}_C$ was calculated and values for activity of carbon could then be found. A plot of these results has also been shown in Graph 11.

The /

The reliability of the values obtained is however doubtful in view of the fact that the error in $\overline{\Delta H_c}$ is given as $\pm$ 1000 cal/mole and a wide discrepancy in carbon activity values would be obtained by calculations using the upper and lower limits of the $\overline{\Delta H_c}$ value. It would appear significant that these calculated results correspond to a simple smooth curve obtained by extending the graph of log γ_c against N_c up to saturation. Whether or not the simplest curve is the correct one remains unknown.

CONCLUSION

It has been shown that most of the experimental work carried out has given results up to 1 - 2 per cent carbon and that carbon in iron obeys Henry's Law up to only 0.02 N_c. There is in fact considerable agreement as to the /

the carbon activity values at low carbon contents, but in the medium to high carbon range there is a serious lack of reliable experimental results. In order to overcome this various attempts have been made to forecast behaviour, at high contents, on theoretical grounds. It has been shown, however, that in all these cases only reliable experimental evidence can show which, if any, of these predictions are justified. It has been shown that some of the assumptions made are unlikely to be correct and that the various expressions derived to represent the behaviour of the iron-carbon melts are not compatable with one another. Thus while attempts to represent the activity of carbon in iron as a mathematical function, applicable at all temperatures and compositions, may be desirable they will require to be based on stronger evidence than is at present available.

CHAPTER III

EXPERIMENTAL TECHNIQUE

Preliminary Discussion

The object of the present work was to study the activity of carbon in liquid iron over a range of carbon contents up to carbon saturation. A temperature of 1450°C was chosen for the initial experiments since at this temperature a wide range of liquid compositions from approximately 1 per cent up to 5.02 per cent carbon, could be studied, this latter composition representing carbon saturation at 1450°C [4]. It was, however, hoped to carry out further studies at higher temperatures if satisfactory results were obtained at 1450°C.

Of the methods available for the activity determination, those involving gas-metal equilibria were considered to be the most accurate in view of the findings of previous workers /

workers in this field. It appeared that the choice should be made between the carbon monoxide - carbon dioxide and the hydrogen - methane equilibria, which may be expressed as shown.

$$CO_2 + \underline{C} = 2CO \quad \ldots\ldots (1)$$

$$2H_2 + \underline{C} = CH_4 \quad \ldots\ldots (2)$$

The disadvantages of reaction (1) for a study at high carbon contents are as follows:-

(a) The ratio of carbon dioxide to carbon monoxide is so low that it is very difficult to control.

(b) A change in the carbon dioxide - carbon monoxide ratios can occur by carbon deposition, as the gases leave the hot zone of the reaction chamber

$$2CO = C + CO_2$$

or by thermal segregation of the gas mixture in the reaction tube.

(c) /

(c) The gas - metal reaction is very slow in reaching equilibrium.

(d) There is the danger of solubility of oxygen in the melt affecting the carbon activity.

Reaction (2) also presents certain difficulties. On studying the equilibrium constant of the reaction one of the main disadvantages of this reaction becomes apparent.

$$2H_2 + \underline{C} = CH_4$$

$$K = \frac{pCH_4}{pH_2^{\,2} \times a_c}$$

$$\Delta G^\circ = -RT \ln K \qquad \Delta G^\circ_{1723} = 23{,}500 \text{ cal/mole} \quad (22)$$

$$23{,}500 = -4.575 \times 1723 \log K$$

$$\therefore K = 1.04 \times 10^{-3}$$

Therefore at carbon saturation (a_c equal to unity), where the maximum amount of methane is formed.

K /

$$K = \frac{pCH_4}{pH_2^2} = 1.04 \times 10^{-3}$$

The equilibrium thus corresponds to only 0.1 per cent methane in hydrogen at 1450°C. Thus, if the hydrogen - methane equilibrium is to be used to study the activity of carbon, it is necessary to carry out measurements of the very small amounts of methane formed with sufficient accuracy to follow slight changes in the methane content as the carbon concentration varies.

The other disadvantage in reaction (2) is because in work of this kind a metal oxide crucible is generally used to contain the melt. This can result in the formation of carbon monoxide by the reaction between the carbon in the melt and the metal oxide. If reaction (1) is being used, any small quantity of carbon monoxide so formed is insignificant /

insignificant compared to the large partial pressure of carbon monoxide introduced into the furnace. When using reaction (2), however, even slight crucible reaction will produce partial pressures of carbon monoxide comparable to those of methane thus complicating the gas analysis problem and perhaps affecting the final gas - metal equilibria.

These disadvantages, namely the measurement of small amounts of methane and the danger of crucible reaction, must be overcome if reaction (2) is to be used. The overwhelming advantage, however, of this reaction, is that the temperature coefficient of the hydrogen - methane equilibrium is such that there is no dissociation of methane with decreasing temperature, and there is therefore no variation between the amount of methane formed /

formed in the hot zone of the furnace and the amount which is finally analysed. Since the disadvantages of the carbon monoxide - carbon dioxide equilibrium become increasingly formidable at high carbon contents, it was decided to use the hydrogen - methane equilibrium to study the carbon activity, while bearing in mind the difficulties already mentioned.

In carrying out this study the first essential was to establish a suitable analytical technique since only then could the results of the equilibrium studies be interpreted. If a suitable analysis technique was not developed at the outset it would be very difficult to determine whether or not any variation in the experimental results was due to the inaccuracy of the analysis technique, failure to reach equilibrium or the interference /

interference of the crucible reaction.

Since normal gas analysis techniques are not efficient enough to measure accurately the small amounts of methane formed, some other technique must be used. There are a number of possibilities for such measurements, including infra-red gas analysis, gas chromatography, gas spectrometry or a radioactive tracer technique. Of all these methods the one which offered the highest inherent accuracy for the estimation of small quantities of carbon in the gas phase was that involving a radioactive tracer. Since carbon has a suitable radioactive isotope it was decided, in the first instance, to try to develop a technique of this type for the estimation of methane.

Radioactive Tracer Technique

Three radioactive isotopes of carbon are known namely /

namely C^{10}, C^{11} and C^{14}. C^{10} and C^{11}, however, have very short half-lives and are unsuitable for most research purposes. C^{14}, on the other hand, is a very useful tracer element, its properties being summarised in the table below

	Isotopic Mass O^{16} = 16.0000000	Nuclear spin	Radiation	Max. Energy (In MEV)	Half Life (Yrs)	Usual Production
C^{14}	14.00767	o	β -	0.154 ± 0.004	5,100	$N^{14}(n,p)$

The long half-life of C^{14} precludes any difficulty due to alteration in the specimen activity over any conceivable experimental period. As can be seen from the table, C^{14} emits no γ-rays, but only soft β particles which are easily shielded during experimental operations. However, the small penetrating powers of the radiation necessitate some special techniques for measuring the radioactivity.

Various /

Various types of counters can be employed to measure the intensity of β radiation. Of these, the most widely used, and the most straightforward type of instrument is the Geiger-Müller tube, and this was chosen for the present work. There are two techniques possible using a Geiger-Müller tube. In the first of these the radioactive source is located outside the tube and the radioactive particles enter the tube by means of a thin window which is more or less transparent to the radiation. This is termed, for obvious reasons, end-window counting. The alternative is to use a tube into which the radioactive sample is introduced in the form of a gas. In order to use this technique, apparatus is required to enable the counting tube to be filled with a suitable gas mixture of accurate composition. For this reason end-window counting appeared to be the simpler /

simpler technique requiring little equipment and no complicated apparatus.

Radioactive Measurement by means of an End-Window Counter

The end-window counting tube used in this study was of type "E.W.3 H." supplied by 20th Century Electronics Ltd. This is a halogen quenched low voltage unit with an operating plateau between 550 - 700 volts, the end-window being of mica 1.5 - 2.5 mg/cm^2. This particularly thin window is essential for low energy β particles. The counting unit was an Echo-Scaler Type "N 529 C" which is a five decade Scaler using "Dekatron" tubes, the output voltage being variable over two ranges 250 - 1000 volts and 500 - 2000 volts, indicated on a meter. In this Scaler positive pulses are fed into an amplitude discriminator and a pulse shaping circuit.

Shaped /

Shaped pulses above a pre-set amplitude are applied to a chain of five triod coupled "Dekatron" tubes. An Echo "N558" Probe Unit was included in the circuit to introduce a known "dead time" after each registered pulse. This is achieved by reducing the potential applied to the centre wire of the tube by some 200 volts for 200, 300, 400 or 500μs (or 1000μs by suitable adjustment of the instrument). This allows a correction to be applied to the measured count rate, making allowance for emissions while the counter is insensitive following the registration of a pulse. This reduction in the total voltage also counteracts the phenomenon of multiple discharge within the tube giving a longer and flatter operating plateau. Multiple discharge results from emission by the cathode of secondary electrons due to positive ion bombardment following the initial discharge /

discharge and reduction of the tube voltage prevents such secondary electrons from reaching the anode.

Since, as will be discussed later, it was intended to count the C^{14} in the form of a solid sample a Sample Chamber Type "N 619" combined with a Geiger-Muller Tube Holder Type "N 620" was used. The Sample Chamber consisted of a cast lead chamber with a hinged lead door. The interior of the chamber is lined with Perspex to minimise "scatter" effects and five pairs of grooves were milled in the side walls, allowing samples to be located at different distances from the end-window of the counting tube which was placed in an aperture at the top of the chamber.

The most accurate method of end-window counting is to have the sample in the form of a very thin layer of powder /

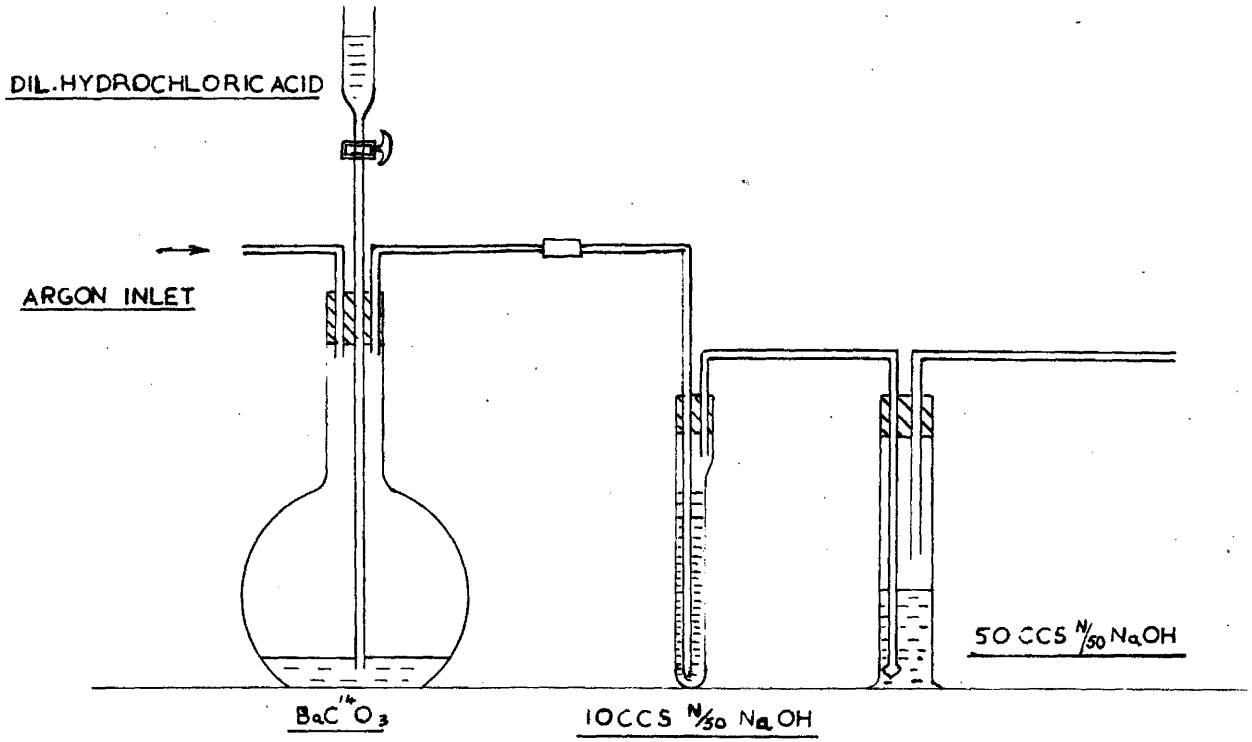


FIG 1. PREPARATION OF RADIOACTIVE SOLUTION

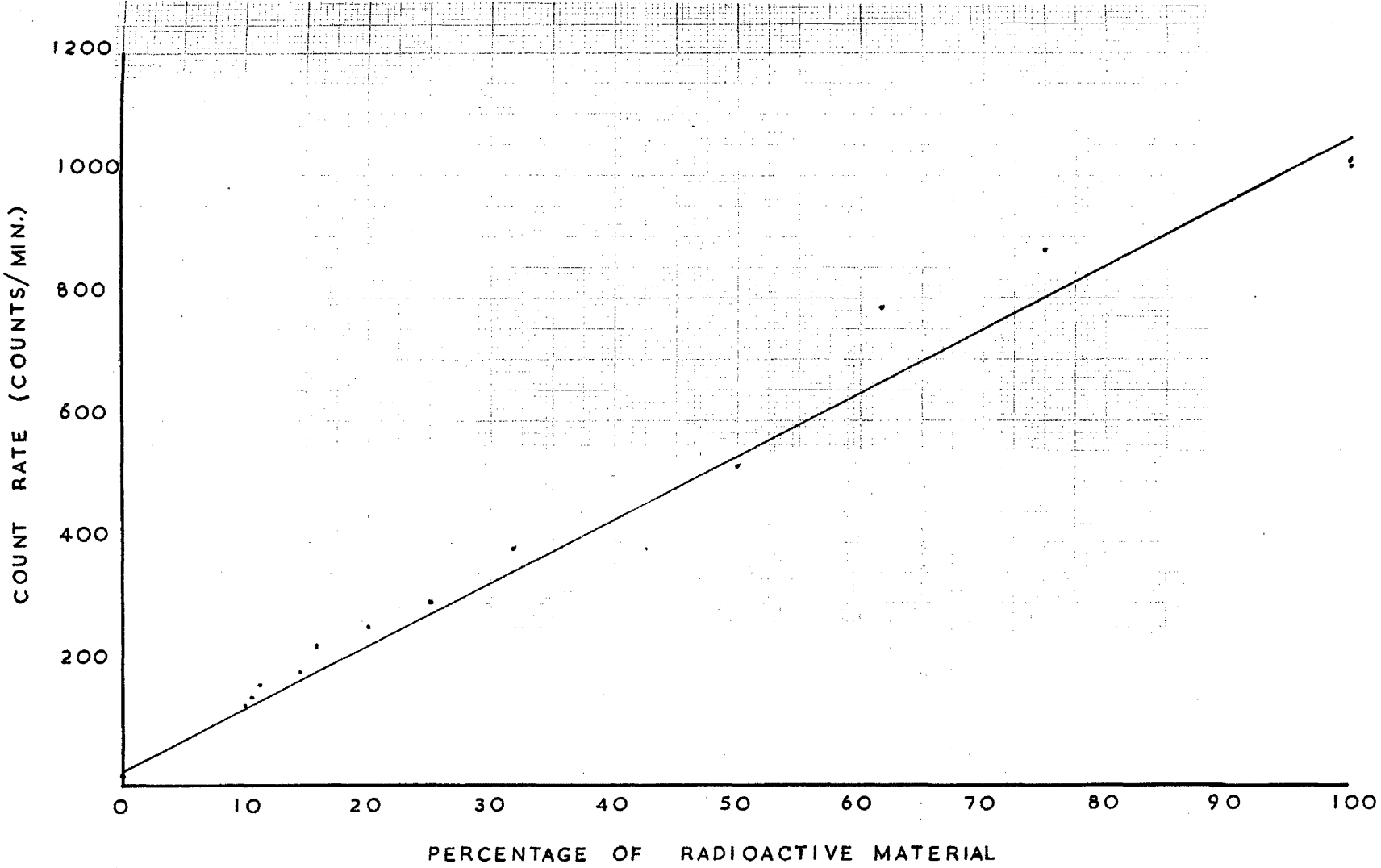
powder. In the present study it was decided to obtain a sample in this form in the following manner. The radioactive methane formed by passing hydrogen over the radioactive melt would be converted to carbon dioxide while simultaneously oxidising the hydrogen by passing the gas mixture through copper oxide at 500°C. The carbon dioxide would then be bubbled through a solution of sodium hydroxide and the resultant sodium carbonate dried to form a powder suitable for counting.

In order to determine whether a suitable end-window counting technique for C^{14} could be developed on these lines, a series of experiments was carried out as described below.

Radioactive carbon dioxide was prepared by use of the simple apparatus shown in Fig. 1. A fixed quantity of radioactive /

radioactive barium carbonate (specific activity 5μc/mM) was placed in the bottom of the flask and hydrochloric acid (1:1) was allowed to run into the flask. The radioactive carbon dioxide thus formed was carried by an argon flow into the two bubblers containing N/50 sodium hydroxide. The first bubbler was specially designed to contain only 10ccs of the solution while still giving intimate contact between the gas and the solution. This served to remove the bulk of the carbon dioxide in as small an amount of solution as possible so that the specific activity of the solution would not be undesirably low. The second gas jar contained 50ccs of sodium hydroxide to remove the remainder of the radioactive carbon dioxide.

One cc samples were drawn from the radioactive solution /



GRAPH III LINEARITY OF RELATIONSHIP BETWEEN C^{14} CONTENT AND COUNT RATE IN END-WINDOW COUNTING

registered in the Geiger-Muller tube. Absorption by the end-window itself while cutting down the number of counts is a constant factor, whereas self-absorption in the powder layer depends on the powder thickness, the distribution and also on the composition of the powder.

In order to determine if the count rate was proportional to the amount of radioactive material present, mixtures containing varying proportions of the radioactive sample and pure N/50 sodium hydroxide were prepared, from which 1cc samples were drawn and counted as already described. The results of these experiments are shown in Graph 111. It can be seen from the graph that, although it approximates to a linear relationship, there is considerable scatter of the points. In order to obtain

a /

a criterion for the linearity of the relationship, the correlation coefficient, r, for the results was obtained, the value being 0.9958. In view of the scatter observed, it was decided to test the reproducibility of the results by measuring the count rate given by a number of 1cc samples drawn from the same radioactive solution. It can be seen from the results given in Table A that there is maximum error of ± 10 per cent on the mean value of the results. This was considered to be undesirably high.

Table A Count rates on 1cc samples of radioactive solution

Sample	1	2	3	4	5	6	7	8	Mean
Counts/ min.	92	97	84	92	95	103	95	97	94.3
%Deviation from the mean	-2.4	+2.9	-10.9	-2.4	+0.7	+9.2	+0.7	+2.9	-

This variation might be due to the distribution of the powder over the area of the planchette, altering the self /

self absorption from sample to sample. In order to improve the distribution of the specimen powder, a drop of "Teepol" was placed on the planchette prior to the addition of the 1cc sample in the hope that the detergent solution, by decreasing the surface tension of the droplet, would give a more even spread of the liquid and hence of the resultant powder. The results of five such tests are given in Table B from which it can be noted that there appears to be little improvement in the scatter which is ± 9 per cent of the mean.

Table B Count rates on 1cc samples of radioactive solution in "Teepol"

Sample	1	2	3	4	5	Mean
Counts/ min.	83	89	97	99	87	91
%Deviation from the mean	-8.8	-2.2	+6.6	+8.8	-4.4	-

These experiments indicated that the end-window technique /

technique would require refinement if results of the desired accuracy were to be obtained. The basic reason for the poor reproducibility is almost certainly due to the low energy of the radiation from the C^{14} which makes the method more sensitive to small variations in the specimen geometry than in the case of an isotope emitting high energy radiation. It is possible that the accuracy might be improved by the use of other sample preparation techniques, however, there is another disadvantage which became apparent during these experiments. The count rates measured by the end-window counter were very low compared to the specific activity of the solution which had been prepared. If this technique was to be applied to the determination of the thermodynamic activity of carbon in iron, a melt of very high specific radioactivity would be required since only /

only a very small quantity of the C^{14} would be converted to methane and subsequently to carbon dioxide. The radioactive carbon dioxide would then be further diluted, since only a fraction of the absorbing solution would be removed for counting. From such a process it can be seen that the specific radioactivity of the sample finally counted would be much lower than the initial activity of the melt, and in order to obtain counts of a significant level compared to background radiation, an extremely high specific radioactivity in the melt would be necessary. This is undesirable since the danger involved in handling the radioactive material is increased.

It was, therefore, decided to endeavour to adopt a gas counting technique. While requiring additional apparatus /

apparatus for handling the radioactive gas, this technique has the advantage of being 90% efficient compared with the end-window counter which is approximately 10% efficient. Since the gas is actually contained within the counting tube, there is little or no loss of the β particles by self absorption or by absorption by a mica window. The other difficulties referred to in the end-window counter are also obviated by a technique of this type.

Gas Counting Technique

Gas counting can be carried out by one of two methods, namely the "non self-quenching" counter or by the "self-quenching" counter. In the former type the phenomena of multiple discharge, which has been discussed above, is prevented by means of an external quenching circuit./

circuit.

However in the present study it was decided to use a "self-quenching" counter where the filling gas consists of a simple gas together with an organic vapour such as carbon disulphide or alcohol. When the positive ion of a large polyatomic molecule comes up to the cathode wall, the molecule will, in general, dissociate rather than release secondary electrons from the metal cathode. Thus by having an organic vapour present in the filling gas, secondary electron emission by positive ion impact may be eliminated and with it the necessity of an external quenching circuit. However since it is difficult to obtain a vapour having ideal characteristics with reference to both positive ion interchange and efficient molecular dissociation /

dissociation an electronic quenching circuit is also desirable. The most successful combination is not, therefore, a true "self-quenching" counter.

The counter tube used throughout the investigation was of Type "GA 10M", which has stainless steel cathode and is 380 x 30 mm overall size. This was used together with the Scaler already described, the probe unit being adjusted to 1000μs. The voltage at which the tube shows its operating plateau depends on the composition and pressure of the filling gas. Due to the fact that the output voltage of the Scaler unit was limited to 2000 volts (it could be used up to 2075 volts) a suitable gas mixture had to be selected. Since the apparatus had been already arranged to remove radioactive carbon from the gas mixture in the form of carbon dioxide /

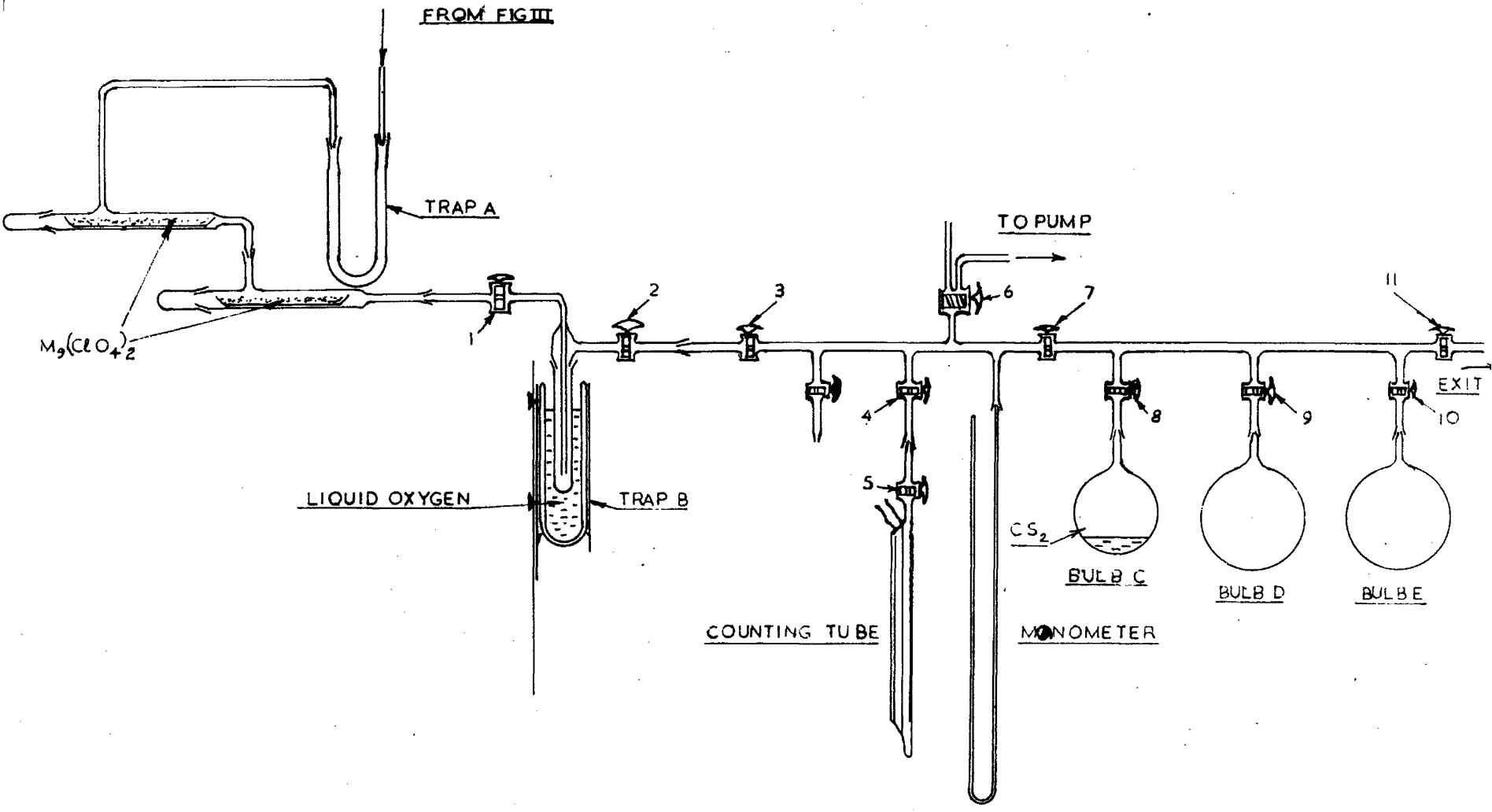


FIG. II APPARATUS FOR FILLING THE GAS-COUNTING TUBE.

dioxide it was convenient to retain the carbon in this form for gas counting. Counting of carbon as carbon dioxide has been investigated by Eidenoff [26] who showed that satisfactory results could be obtained over a wide range of pressures and voltage, in the presence of carbon disulphide as a quenchant. From this work it appeared that 4 cms Hg pressure of carbon dioxide together with 2 cms Hg of carbon disulphide would be a suitable mixture for work up to 2000 volts.

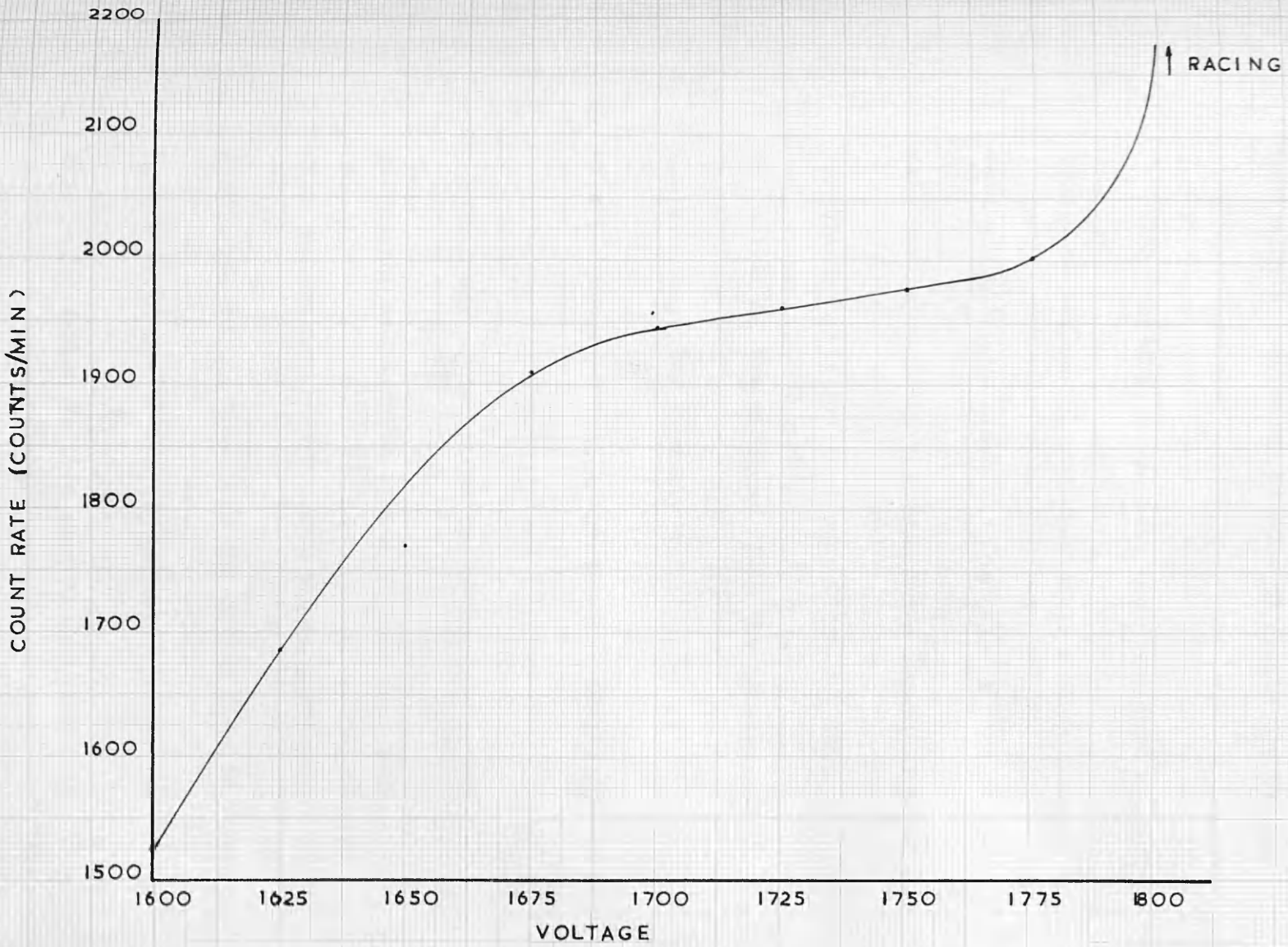
The arrangement for filling the counting tube is illustrated diagramatically in Fig. II. The radioactive carbon dioxide was passed through trap (A) immersed in a mixture of alcohol and "Dricold" to remove the water vapour present and any residual vapour was removed in the two drying tubes containing alundum boats filled /

filled with magnesium perchlorate. The carbon dioxide was condensed in a trap (B) which was immersed in liquid oxygen. The vacuum line between taps (1) and (11) was then pumped down to 0.001 mm Hg by means of a two stage rotary pump, prior to allowing the carbon dioxide to volatilize and fill the system. If more than 4 mm Hg pressure was present the carbon dioxide was again frozen out by means of the liquid oxygen. It was again allowed to volatilize and when 4 cm was present tap (3) was closed. If, on the other hand, less than 4 cm Hg of carbon dioxide was present it was made up to 4 cm Hg by means of non-radioactive carbon dioxide from Bulb (D) which had been previously filled from a cylinder. 2 cm Hg of carbon disulphide was then added by manipulating the tap above the carbon disulphide bulb. After allowing the gas to mix for

two /

two or three minutes tap (5) on the counting tube was closed and the system was pumped down. The exit gases from the pump were led through a sodium hydroxide bubbler to prevent any danger of radioactive gas escaping to atmosphere. After tap (4) was closed, the counting tube was disconnected from the vacuum line and taken to the counting apparatus.

In order to reduce the "background" counts to a minimum a lead "castle" was prepared by casting lead into the annulus between steel tubes of $4\frac{1}{2}$" and $1\frac{1}{4}$" diameter. The counting tube was placed in this "castle" prior to counting. A check on the background count was made by filling the tube with 4 cm Hg carbon dioxide from Bulb (D) and adding 2 cm Hg of carbon disulphide from Bulb (C). The background count was generally /



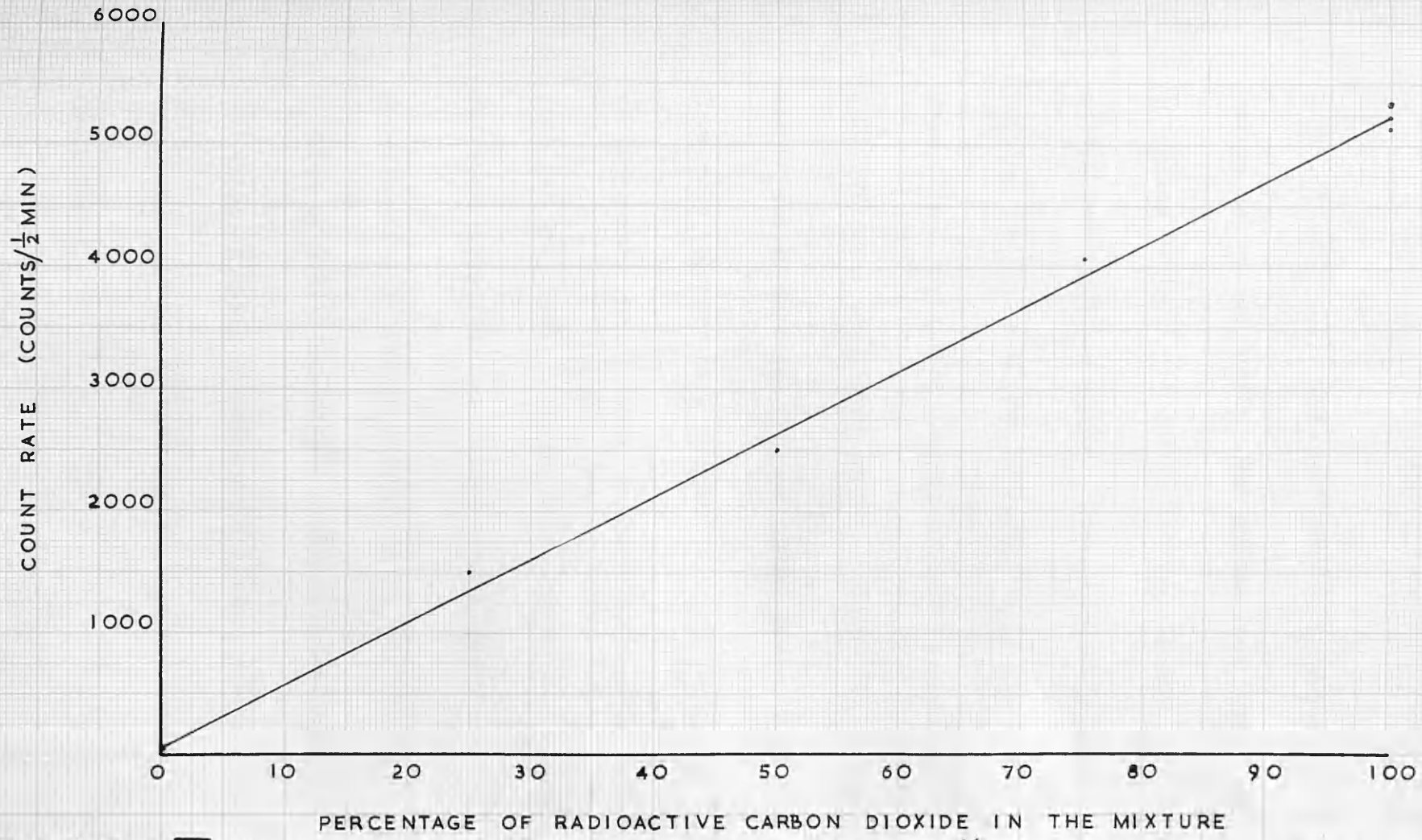
GRAPH IV TYPICAL PLATEAU OBTAINED WHEN GAS COUNTING

generally of the order of 60 - 80 counts per minute.

When counting the plateau was determined by taking counts at increasing voltages until racing occurred (i.e. when a continuous discharge formed). A plot of count rate against voltage was then drawn (Graph 1V being a typical example) and the count taken was that obtained two thirds of the distance along the plateau. The plateau range was normally of the order of 75 volts with a slope over that range of approximately 5 per cent.

In order to determine the efficiency of this technique, radioactive carbon dioxide was prepared from radioactive barium carbonate as previously described, but in this case the carbon dioxide carried in the argon stream was introduced into the gas counting line. The carbon dioxide present was frozen out in

trap /



GRAPH V LINEARITY OF RELATIONSHIP BETWEEN C^{14} CONTENT AND COUNT RATE IN GAS COUNTING

trap (B), (Fig. 11), the argon passing through the system and out at tap 11. The system from taps 1 - 11 including Bulb (E) was evacuated with the condenser (B) surrounded by liquid oxygen. After some five minutes pumping the pump was shut off, the liquid air trap removed and the carbon dioxide allowed to fill Bulb (E). Mixtures containing varying proportions of the active gas in Bulb (E) and the normal carbon dioxide from Bulb (D) were then prepared and counted. A plot of the results can be seen in Graph V. It can be seen from the Graph that a linear relationship is obtained and that the points fit the curve very well. The correlation coefficient calculated in this case gave a value of 0.9995 which is a distinct improvement in the value of 0.995 obtained with the end-window technique. It did in fact appear that any slight deviation /

deviation from the line could be attributed to the difficulty of obtaining very accurate pressure measurements while filling the tube with the constituent gases rather than any defect in the counting technique. This is substantiated by the fact that the reproducibility in successive samples was of the order of $\pm$ 2 per cent, which corresponds to an error of $\pm \frac{1}{2}$ mm in the manometer readings when the gas samples are introduced into the counting tube.

By this method much higher count rates were obtained with the same quantity of radioactive carbon as had been used in the end-window technique. It appeared that a highly successful counting technique had been developed which would enable accurate determinations to be made of the radioactive gas formed when passing

hydrogen /

hydrogen over a radioactive melt.

It was intended to utilise the radioactive technique by bringing to equilibrium with hydrogen a melt containing some radioactive carbon and with a total carbon content equivalent to saturation at the desired operating temperature. The count rate determined on the methane formed during this experiment may then be considered to represent unit activity, since the standard state chosen is that of carbon saturation. Subsequent melts of lower carbon content may then be prepared by dilution of the original melt with carbon free iron. This does not alter the specific activity of the carbon present and, therefore, the ratio of the count rate obtained on equilibrating a lower carbon melt to that obtained for saturation is equivalent to the ratio of the methane /

methane contents in the two cases. Activity of the carbon is thus measured directly.

An apparatus in which experiments of this type could be performed was assembled.

Crucible Material

In view of the danger, discussed earlier, of crucible reaction affecting the results obtained, careful consideration was given to the choice of crucible material. This topic is fully discussed later. Alumina crucibles were used in most of the experimental work since, apart from theoretical considerations, these crucibles have the advantages of high purity and of being readily available in an extremely well shaped and fired condition. In some experiments alumina

was /

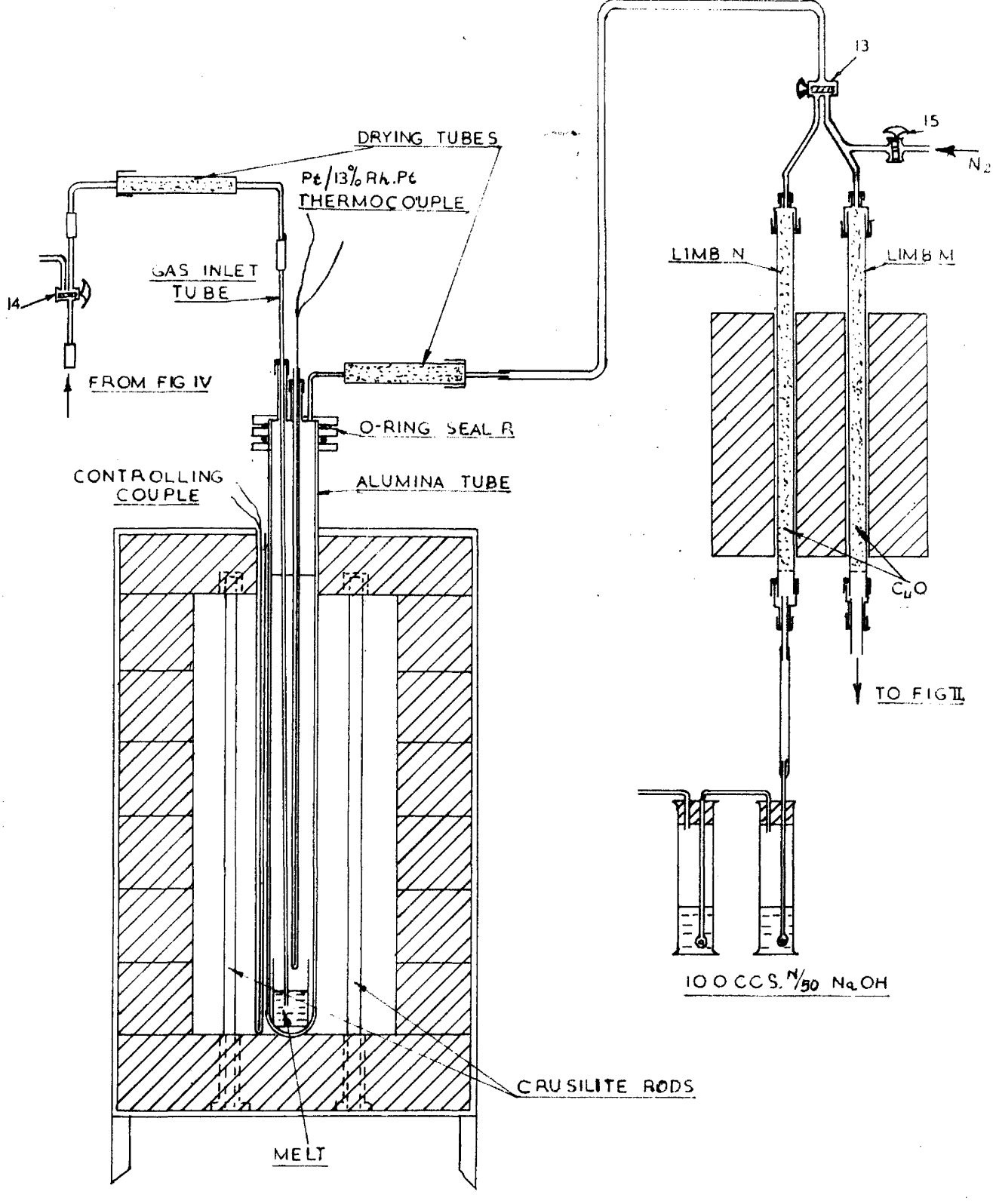


FIG III CRUSILITE FURNACE, REACTION CHAMBER & COPPER OXIDE FURNACE

was replaced by boron nitride or beryllia crucibles.

Furnace and Reaction Chamber

The furnace and reaction chamber are illustrated diagramatically in Fig. 111. A furnace heated by four silicon carbide resistance elements ("Crusilite" Type "DS") was used to give a temperature of 1450°C. The advantages of this form of heating are that a temperature of 1450°C can be reached quickly, a long hot zone is obtained (a drop of 1½°C over a 3" length being obtained with the present furnace), and the elements are unaffected by intermittent use of the furnace.

A refractory tube 59 mm external diameter, 50 mm internal diameter, 560 mm long and closed at one end was inserted in the furnace and used as the reaction chamber /

chamber.

The power input into the furnace was controlled by a 30 amp Variac autotransformer. The temperature was regulated by a "Kelvin Hughes" controller which was connected to a platinum / 13 per cent rhodium - platinum thermocouple housed in a mullite (or alumina) thermocouple sheath positioned against the outside of the reaction chamber. Obviously this control couple did not give an accurate measurement of the melt temperature and this was measured accurately by a platinum / 13 per cent rhodium - platinum thermocouple in a sheath inserted into the reaction chamber and held just above the melt. The e.m.f. generated by the thermocouple was measured by a "Cambridge" potentiometer. The hot zone under conditions approaching those during the experimental runs was determined /

determined by the normal technique of raising and lowering the thermocouple within the reaction tube and measuring the temperature. This enabled the temperature of the melt to be accurately determined by making allowance for the distance of the thermocouple from the surface of the melt. The thermocouple was also standardized against the melting points of gold (1063°C) and palladium (1555°C). By using these correction factors and by suitable adjustment of the controller it was possible to maintain the temperature at 1450 ± 5°C quite easily over long periods.

In the initial experimental runs a mullite reaction tube was used with mullite thermocouple sheaths, but, for reasons which will be discussed later mullite was replaced by recrystallized alumina refractories in most of the runs. Whatever the refractory material used the arrangement /

arrangement was the same. The top of the furnace tube was sealed by means of high temperature O-rings (Sil 160) compressed on to the walls of the tube by the brass top and ring clamps (R) shown in Fig. 11. The inner thermocouple sheath (600 mm long, 10 mm external diameter and 6 mm internal diameter) and the gas inlet tube were sealed to the brass top by O-rings. The latter tube (800 mm long, 6 mm external diameter and 3 mm internal diameter) entered the reaction chamber at a slight angle so that it dipped into the melt without touching the thermocouple sheath.

Initially the brass top of the reaction chamber was cooled by a water cooled copper coil round the top 6" of the reaction tube. This, however, resulted in a number of tubes being cracked since water condensed on the /

the copper tube and dropped on to the hot refractory material. The water cooling system was replaced therefore by a radiation shield consisting of a piece of platinum foil suspended 6" from the top of the tube. This proved to be quite satisfactory provided high temperature silicone O-rings were employed.

The crucible, normally containing 50 gm of metal, was set in the hot zone of the tube by placing it on an alumina stool of appropriate height. The stool sat on the bottom of the reaction tube but latterly a stool was placed externally under the base of the tube and the hot zone was then so near the bottom of the tube that no internal stool was necessary. The thermocouple sheath was lowered to a fixed distance from the metal surface and the O-ring joint was tightened. The gas inlet tube could /

could then be adjusted so that the gas bubbled through the melt or played on to the metal surface from any fixed distance above the melt. The positioning of the gas inlet tube will be discussed later.

Great care had to be taken to ensure that the whole of the reaction chamber was gas tight since any inleakage would have led to oxygen contamination in the furnace gases and leakage outwards would also have been particularly dangerous due to the possibility of radioactive gases escaping.

Gas Purification Train

The gases used during the experimental runs were high purity hydrogen and high purity nitrogen or argon. These gases, as supplied, were all stated to contain less than /

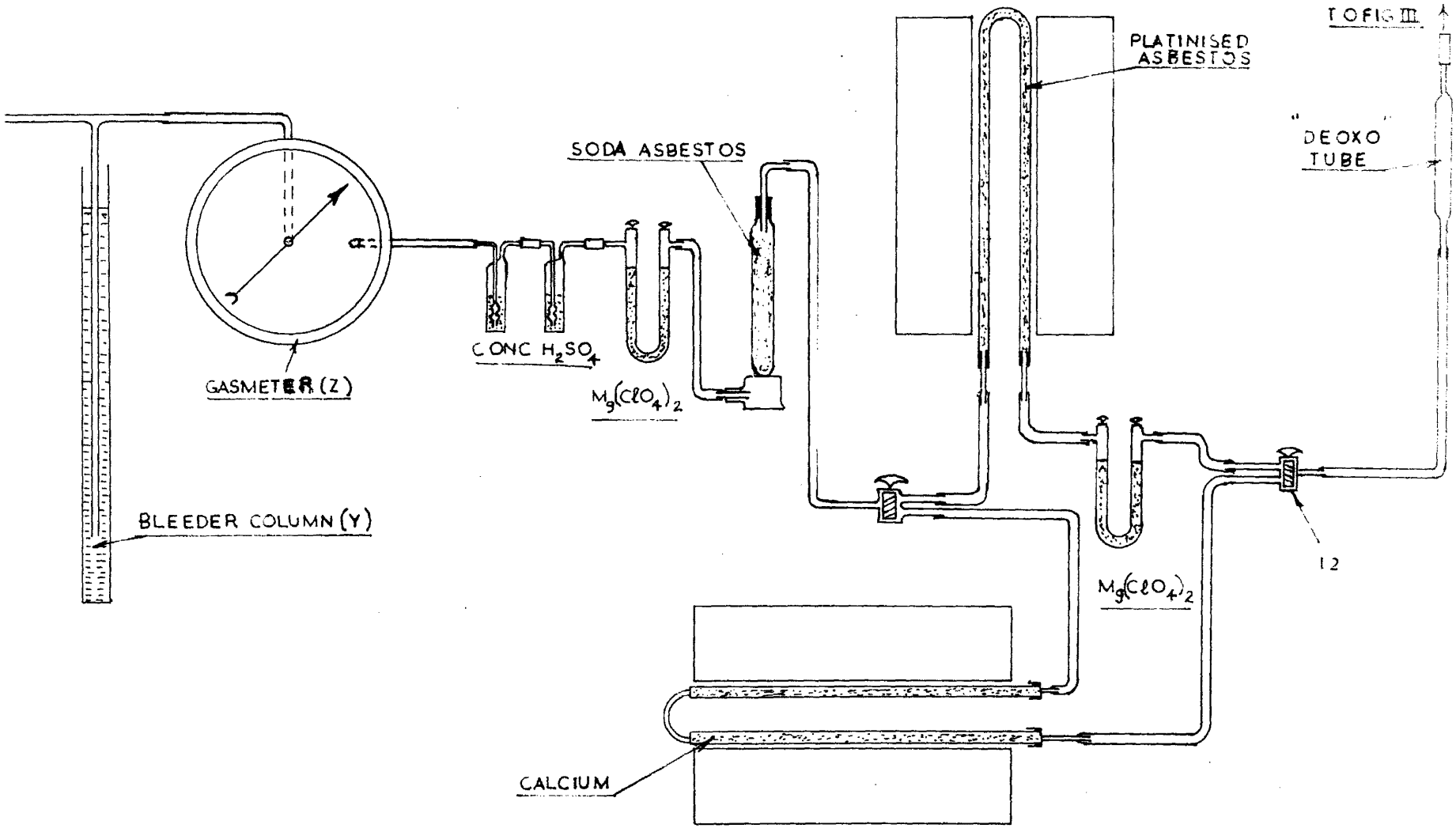


FIG V GAS PURIFICATION TRAIN

than 10 v.p.m. oxygen, however, in order to ensure that the gases were as pure as possible they were passed through the purification train illustrated diagramatically in Fig. 1V. The gas was passed across a bleeder column (Y), where by adjustment of the water level, the flow rate of the gas through the system could be regulated. The gas was then passed through the gas meter (Z), where the volume of the gas could be carefully measured. This meter prior to use was checked by means of a water displacement technique and found to be very accurate. Since the gas had picked up water vapour in these stages it was then passed through concentrated sulphuric acid and through a U-tube containing magnesium perchlorate. Any carbon dioxide present in the gas was removed by a tower containing soda asbestos. At this stage the purification train was split in two, one part for the purification of hydrogen /

hydrogen and the other for the purification of nitrogen and argon.

In the hydrogen purification train the gas was passed through a tube containing platinised asbestos at 300°C. The platinised asbestos was interspersed with small silica chips to avoid any danger of the platinised asbestos choking the tube when the gas flowed through. Platinised asbestos catalyzes the combination of hydrogen and any oxygen present to form water vapour, this being removed by a U-tube containing magnesium perchlorate.

The purification of the argon and nitrogen was achieved by simply passing the gas through a stainless steel tube containing calcium turnings at 680°C, any oxygen present being thus converted to calcium oxide and hence removed from the inert gas.

The /

The two way tap (12) allowed the gas from either of the purification trains to be passed, subsequently, through a "Deoxo" tube which is also a catalytic method for hydrogen purification. The gases then entered a copper chamber containing a drying agent, either magnesium perchlorate, or in later runs a molecular sieve, material Type "5A". The reason for using this metal drying chamber immediately prior to the reaction tube was that all the connections in the purification train were of either rubber or polythene and figures quoted by Barrer [23] and tests described by Hayward [24] show that these tubes are permeable to water vapour. The copper drying chamber was connected directly to the alumina gas inlet tube by means of a copper tube, the connection being made by "Araldite". This arrangement ensured that no water vapour which permeated through the other connections could enter the /

the reaction chamber.

Copper Oxide Furnace

The gases leaving the reaction chamber passed through another copper drying chamber containing magnesium perchlorate which prevented any water vapour diffusing back into the reaction chamber. The gas was then passed through the furnace containing copper oxide at 700°C to convert the methane to carbon dioxide. Free energy data for the reaction allows the extent of methane conversion to be estimated as shown :

$$CH_4 + 4CuO = CO_2 + 2H_2O + 4Cu$$

$$K = \frac{pCO_2 \times pH_2O^2}{pCH_4} \qquad \Delta G^\circ_{1000} = -126,480 \quad (22)$$

$$\log K = 27.7$$

$$K = 10^{27.7}$$

This very high value for the equilibrium constant indicates /

indicates that the residual methane content is exceptionally small under equilibrium conditions, so that quantitative conversion to carbon dioxide may be assumed.

The furnace is shown diagramatically in Fig. 111. The fine copper oxide is contained in two silica tubes which are connected to the two-way stopcock (13), by means of O-rings and brass unions. The limb (M) has an inlet tube connected to it in order that nitrogen can be introduced to flush out any radioactive gas left in the tube after each run. The exit end of this limb is connected to the analysis part of the system by another O-ring and brass union joint. The lower end of the second silica tube is connected similarly to two bubbling tubes containing 100 cc of N/50 sodium hydroxide. This limb is merely a by-pass used while flushing out

the /

the reaction chamber.

Preparation of Iron - Carbon Alloys

As discussed previously the purpose of the first experimental runs was to obtain a radioactive count rate corresponding to equilibrium between hydrogen and a melt saturated with carbon at 1450°C, this represents unit activity of carbon. It was necessary, therefore, to prepare a sample of iron containing 5.025 per cent carbon, the saturation value for carbon at 1450°C [4], part of this being in the form of C^{14}. An initial attempt to prepare iron saturated with carbon was made by heating 500 gm of armco iron (analysis : C 0.10 per cent; Mn 0.013 per cent; P 0.005 per cent; S 0.035 per cent; Si a trace) in a graphite crucible at 1450°C in a high frequency furnace. The metal was held at this temperature /

temperature before quenching into water. However, on analysing for carbon it was found to be well below saturation. This appears to be due to some carbon coming out of solution as the temperature fell in the interval between sampling and quenching.

A second attempt was made, the iron being heated again in a carbon crucible but in this case in the experimental furnace already described. After holding the iron at 1450°C for half an hour a silica sampling tube was dipped into the melt and a sample was drawn into the tube by suction and quickly quenched in water. Again, however, the carbon analysis was lower than the saturation value. Thus it appeared that the quench was still not quick enough to prevent carbon coming out of solution.

This problem was finally overcome by preparing a

sample /

sample of iron containing more than 5.025 per cent carbon and mixing this sample with another containing less than the saturation amount. The high carbon sample was prepared by heating 500 gm of armco iron in a graphite crucible to 1550°C by means of a platinum wound furnace. At 1550°C the solubility of carbon is much higher. Again the metal was drawn into silica sampling tubes and water quenched. On drying the metal was analysed for carbon and found to contain more than the necessary 5.025 per cent carbon.

This technique also allowed the problem of introducing radioactive carbon into the melt to be overcome. A radioactive sample was prepared by putting fixed weights of high purity electrolytic iron and graphite powder in an alumina crucible together with 0.2 gm C^{14} (low specific /

specific activity), these quantities being chosen to give a sample of iron containing approximately 2 per cent carbon. This melt was deliberately left well below saturation in order to avoid any danger of loss of radioactive carbon. The melt was heated in vacuo to 1450°C and held for 2 - 3 hours and then allowed to cool in the furnace. The final samples for experimental runs could then be obtained by mixing this radioactive sample with the oversaturated metal in the required proportions to give a radioactive sample of the requisite carbon content.

Dilution of the carbon content for some runs was achieved by simply adding the required amount of electrolytic iron to the saturated sample.

Analysis of Carbon in Iron

The /

The normal gravimetric combustion method [25] was used for the analysis of carbon in iron. 1.362 gm of the powdered alloy was held in a pre-ignited combustion boat for half an hour at 1100°C while oxygen at a rate of 300 ml per minute was passed over the metal sample. The carbon dioxide formed was passed through chromic acid to remove any sulphur gases present, then through concentrated sulphuric acid bubblers and a magnesium perchlorate U-tube to remove any moisture present before finally collecting the carbon dioxide in a midvale bulb containing soda asbestos. The increase in weight of the bulb multiplied by the necessary factors gave the percentage of carbon in the iron. The analysis was checked regularly by means of a British Chemical Standard iron containing 3 per cent carbon.

Gas /

Gas Analysis by Gas Chromatography

For reasons which will be discussed later it became necessary to obtain a gas analysis technique which would differentiate between carbon monoxide and methane in the furnace gases. As indicated earlier, gas chromatography also offers a method of detecting small percentages of such gases, although quantitative estimation is difficult at very low concentrations. The principle of this method is that if a carrier gas containing the gas sample is passed through a molecular sieve the individual constituents in the gas mixture are retarded in the sieve for varying lengths of time depending mainly on their molecular size. A column of this type therefore offers a means of separating the constituents of the gas mixture. If a detecting device is present at the end of the column the individual /

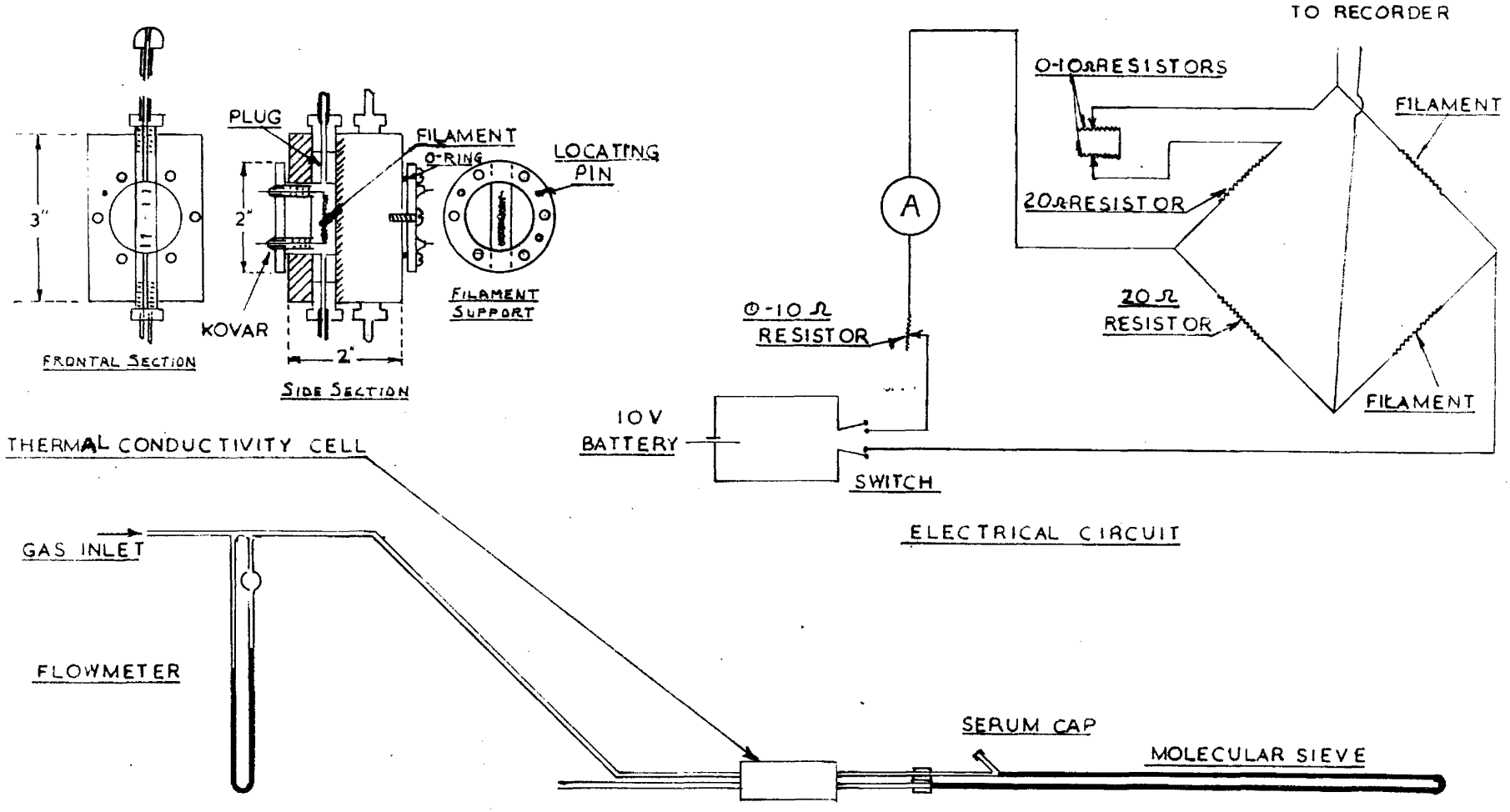


FIG V GAS CHROMATOGRAPHY APPARATUS

individual constituents can be identified and their concentrations estimated by reference to suitable standards. The detection device usually measures the change in some physical property, such as density, viscosity, infra-red absorption, thermal conductivity or heat of absorption, due to the presence of the various constituents in the carrier gas stream. Measurements by means of thermal conductivity, however, have proved to be both reliable and sensitive. An apparatus of this type (27) was constructed in an attempt to identify methane and carbon monoxide in the furnace gases.

The apparatus is illustrated in Fig. V. The carrier gas used was hydrogen flowing at the rate of 100 ml per minute. The hydrogen passed through the reference arm of the thermal conductivity cell and subsequently through /

through the separating column consisting of a 3" length of 1/4" external diameter copper tubing packed with molecular sieve material Type "5A" (dehydrated aluminium calcium silicate) ground to -30 +60 mesh. The gas sample to be analysed was introduced into the carrier gas stream entering the column by means of a hypodermic syringe inserted through a serum cap on the side tube. After passing through the molecular sieve the gases entered the detecting arm of the thermal conductivity cell and thence passed to atmosphere.

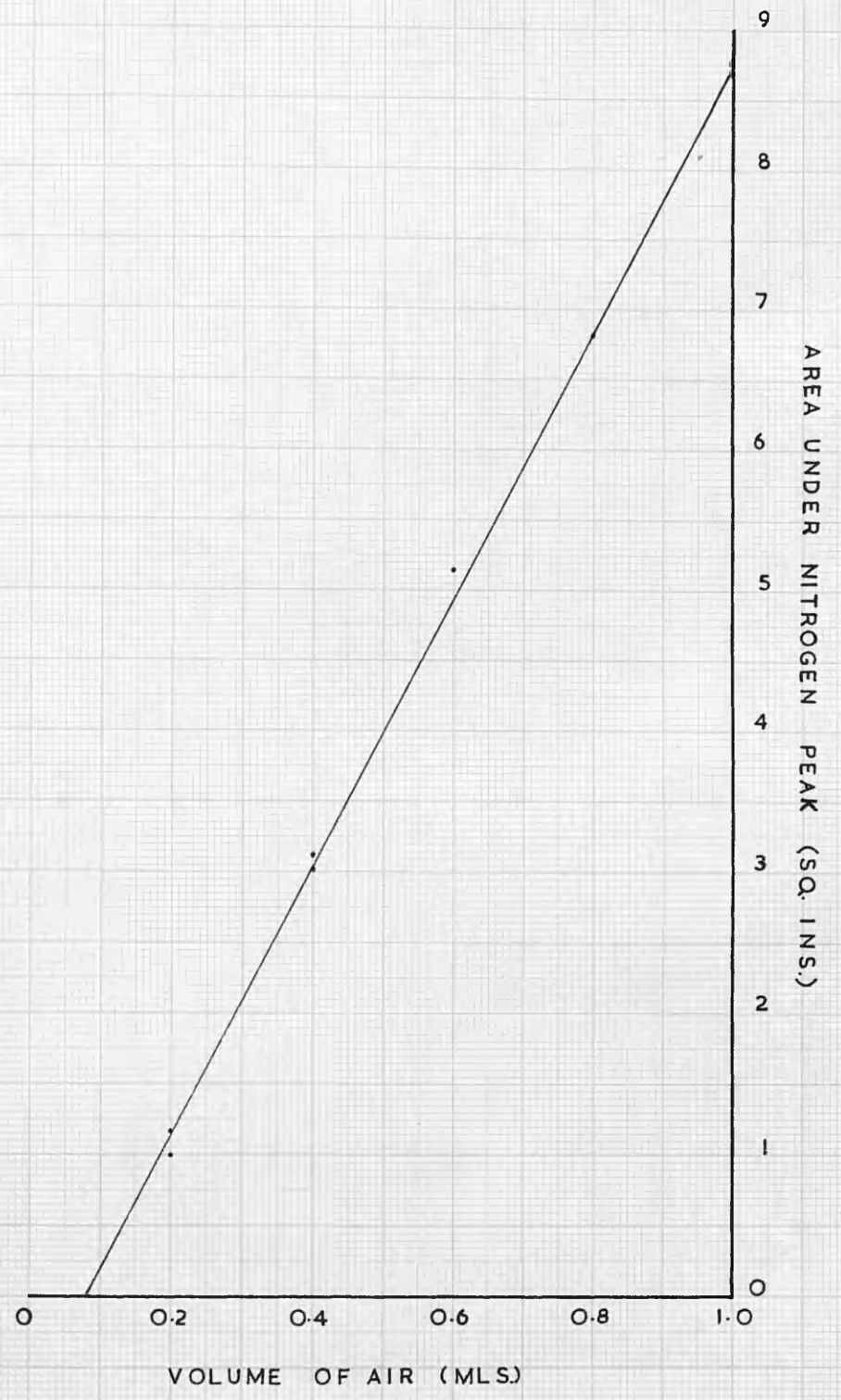
The thermal conductivity cell [27] is illustrated diagramatically in Fig. V. Two similar chambers are machined in a brass block, which because of its high thermal conductivity and large mass acts as a temperature stabiliser. Two identical filaments, each consisting of

a /

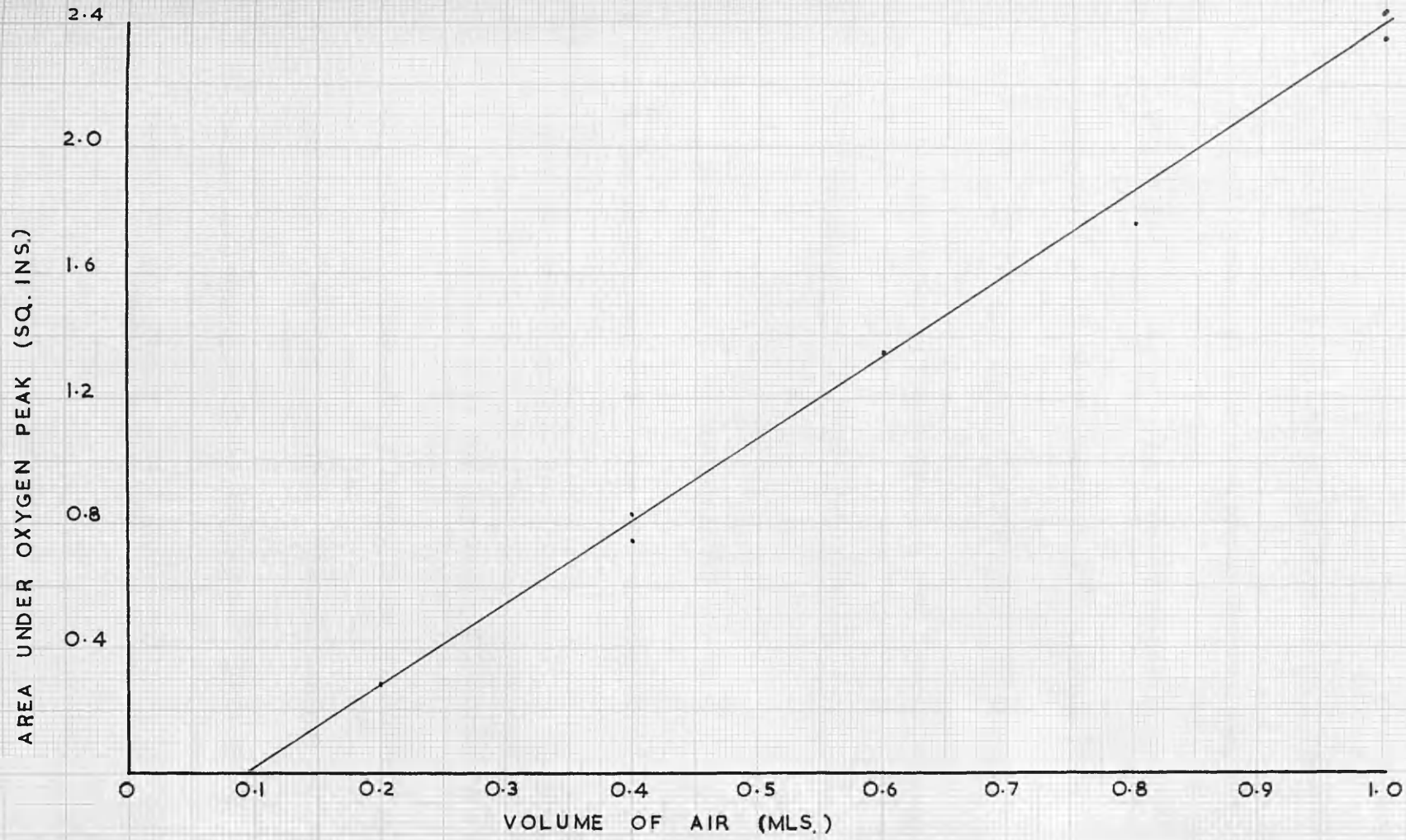
a spiral 0.3 cm in diameter containing 14 cm of 0.005 cm diameter platinum wire, are silver soldered to the ends of insulating terminals mounted on brass caps through which the leads are taken to external connections. The brass caps are sealed by O-rings to the body of the cell so that the filaments are in line with the gas channels.

The electrical circuit which is basically a Wheatstone Bridge arrangement is illustrated in Fig. V. The filaments are heated by the current supplied from the 10v source, the filament temperature being controlled by the variable resistance. Preliminary experiments indicated that a current of 0.66 amps gave a filament temperature which resulted in a suitable response of the filament resistance to variations in the thermal conductivity of the gas in the detecting chamber. The

out /



GRAPH VII CALIBRATION OF GAS CHROMATOGRAPHY APPARATUS FOR NITROGEN



GRAPH VI CALIBRATION OF GAS CHROMATOGRAPHY APPARATUS FOR OXYGEN

out of balance potential of the Wheatstone Bridge circuit, resulting from changes in the resistance of the detecting filament was recorded directly by a "Honeywell" strip chart recorder with a total range of 0 - 10 mv. and characteristic peaks on the trace produced by the recorder enabled both identification and an estimation of the gases present.

The method for determining the volume of gas present is to measure the area under the peak and in order to establish that this area is proportional to the quantity of gas introduced into the apparatus different volumes of air were introduced by means of the hypodermic syringe. A plot of the areas obtained against the volume of gas introduced is shown in Graphs VI-VII from which it can be seen that a linear relationship is obtained.

Since /

Since in the present study it was desirable to detect the presence and amount of methane and carbon monoxide in hydrogen, fixed volumes of pure carbon monoxide and known air-methane mixtures were introduced into the system. The unknown gases could then be identified by comparing the time interval between introducing the gas sample and the point where the individual peaks appeared with that of the known gas sample. Having identified the gas, its volume could then be assessed by comparing the area under the peak with the area for a known volume of the gas. In this manner both carbon monoxide and methane could be identified and measured since they separated quite distinctly.

The amount of methane expected was about 0.1 per cent /

cent in hydrogen and in order to measure such a small quantity of gas in the apparatus available it would be necessary to introduce a very large sample of the gas. As this was impracticable, it was decided to concentrate the gas by removing some of the hydrogen by means of a palladium thimble heated to 250°C through which the hydrogen could diffuse. A 100 cc sample was thus concentrated to approximately 30 ccs and a 10 cc sample was taken and introduced into the chromatography apparatus. By this technique it was possible to detect very small quantities of methane and carbon monoxide but the accuracy of the measurement below 0.1 per cent was poor.

Procedure for Experimental Runs

50 gm of the requisite metal sample was placed in the /

the crucible which was then lowered into the reaction chamber. The reaction chamber was then sealed by means of the brass top and O-rings with the end of the thermocouple sheath positioned just above the metal surface. Before the run was commenced the gas-inlet tube was clamped by its sealing ring in a position well above the metal surface and the reaction chamber and gas analysis apparatus were evacuated. On reaching a suitable vacuum (zero reading on the manometer) the furnace was brought to temperature while purging out the gas purification train with argon or nitrogen and allowing this gas to pass to atmosphere via tap 13. When a radioactive sample was being used particular care had to be exercised so that if any radioactive gas was formed within the furnace it was not allowed to escape to atmosphere via the vacuum pump. For this

reason /

reason the copper oxide furnace was always kept at a temperature of 500°C, to convert any carbon monoxide present to carbon dioxide and two bubblers containing 100 ccs each of N/50 sodium hydroxide were connected to the exhaust side of the vacuum pump.

On reaching the temperature required, the gas-inlet tube was lowered to the appropriate depth, relative to the melt, and the vacuum tap 13 was closed. The inert gas was then allowed to flow into the reaction chamber and on reaching atmospheric pressure the tap 13 was turned to allow the gas to flow down limb (N) containing copper oxide and subsequently into the bubblers containing N/50 sodium hydroxide. The tap to the vacuum pump was closed and nitrogen was passed via tap 15 into the analysis section and out the /

the exit end of the vacuum line. The water freezing jacket (A), containing a mixture of "Dricold" and alcohol at approximately -30°C was brought into position as was the liquid oxygen container to freeze out the carbon dioxide. When these traps were in position the exit tap was closed and the nitrogen turned off prior to closing tap 15, leaving the analysis side of the apparatus filled with nitrogen.

When the necessary amount of gas (2 - 3 litres) had been passed to flush out the reaction chamber, tap 13 was turned so that the gas was passing into the analysis section, the exit tap was opened and a stopclock was started. When two litres of gas as measured by the meter had passed through the system the tap, 13, was turned so that the gas was again flowing down limb (N) of /

of the copper oxide furnace and the stopclock was stopped thus allowing the flow rate of the gas during the run to be calculated. The analysis side was then flushed out by passing nitrogen through tap 15 for five minutes at approximately 100ml per minute.

The choice of two litres of hydrogen was based on a compromise between the size of the copper oxide furnace and the amount of hydrogen required to give a measurable amount of methane. In order to pass a larger volume of hydrogen a greater amount of copper oxide would be required to oxidise the hydrogen and methane and hence a larger furnace would be required. A volume of two litres of hydrogen allowed a number of consecutive runs to be carried out before it was necessary to reoxidise the copper.

When /

When the analysis system had been flushed out the exit tap (11), and tap 1 were closed and this part of the system including the counter tube was pumped down. The tap leading to the pump was then closed, the liquid oxygen trap was lowered and the carbon dioxide condenser was allowed to reach room temperature before reading the pressure on the manometer.

If gas was being counted, tap 3 was closed and the pressure of carbon dioxide was brought up to 4 cm Hg by gas from bulb (D) which had been filled with carbon dioxide from a cylinder prior to the run commencing. 2 cm Hg of carbon disulphide from bulb (E) was also added, the tap 5 was closed and the system was pumped down. Tap 4 was then closed and the counting tube was disconnected and the gas was counted.

The /

The counting tube was then replaced and the whole analysis part of the system was pumped down prior to filling with nitrogen in preparation for another run. Thus a number of consecutive runs could be performed.

The above procedure applied to both the inert gas and the hydrogen runs. At the commencement of a new set of experiments a blank value was usually obtained by passing the inert gas through the reaction chamber. When the blank had reached a fairly constant level the tap prior to the reaction chamber was closed and the reaction chamber and the analysis section was pumped down. Hydrogen was then passed through the purification system, the necessary adjustments being made to the train so that the hydrogen passed through the platinised asbestos furnace rather than the calcium furnace. The gas passed to atmosphere at the tap (14) prior to

the /

the reaction chamber until the purification train was completely purged out. Runs were then performed with hydrogen in an exactly similar manner. If, however, a number of consecutive runs were performed the copper oxide was eventually exhausted, this being indicated by bubbles of gas passing out of the bubblers at the exit end of the analysis section. It was then necessary to re-oxidise the copper and this could be done simply be opening tap 15 and drawing air through the copper by means of the pump. Attempts to re-oxidise the copper by passing oxygen through it resulted in sintering of the copper. This was, of course, because the oxidation of copper is an exothermic reaction but the diluting effect of nitrogen in the air was sufficient to keep the temperature below the sintering temperature.

Another /

Another difficulty with hydrogen runs was the large amount of water frozen out in the trap (A), and after about four runs it was necessary to remove the U-tube and take out the ice formed to prevent the tube becoming blocked.

When the runs were completed the analysis section and the reaction chamber were pumped down while the furnace cooled.

CHAPTER IV

DISCUSSION OF RESULTS

TABLE I

Runs Performed at 1450°C in a Mullite Tube with Carbon Saturated Iron in an Alumina Crucible

Run No.	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R17	R18	R20
Pressure of Carbon Dioxide (cms Hg)	28•3	11•5	3•8	8•8	0•8	0•8	1•4	2•0	3•0	2•5	0•7	6•0	5•0	24•2	38•5	2•5
$p_{CO_2} \times 10^3$ atmospheres	36•79	14•95	4•94	11•44	1•04	1•04	1•82	2•6	3•9	3•25	0•91	7•8	6•5	31•46	51•35	3•25
Flow Rate (ml/min)	160	200	160	120	100	-	300	180	220	180	300	130	140	120	90	320
Count Rate (counts/min)	-	-	-	-	-	315	695	528	905	735	235	1171	-	1120	9750	6183

Discussion of Results and Experimental Difficulties

As has been already stated the initial experimental runs were carried out using a mullite reaction chamber with a carbon saturated melt contained in an alumina crucible. The choice of a high temperature refractory tube was rather limited and in the present work the tubes considered were mullite and alumina and as mullite tubes were less expensive and had just as good physical properties as the alumina tubes, the mullite tubes were used initially to establish a suitable experimental technique. The results of runs using a mullite tube are shown in Table 1. It should be noted that as a different melt was used in each experiment the specific activity of the melts varied and the count rate was therefore correspondingly different from run to run. However, it

can /

can be seen from these results that the carbon dioxide condensed in the apparatus, on expanding to fill the volume between taps 1 and 11 (Fig.II), gave pressure readings which varied from 0.7 to 39.5 cm Hg. As this quantity could be readily measured, it was felt that initially this pressure measurement rather than a radioactive measurement would give a suitable method of comparison until a constant pressure value was obtained for the carbon saturated melt. The volume between taps 1 and 11 was measured and found to be 202 cc. Hence the pressures of carbon dioxide measured on the manometer were converted to equivalent partial pressures of carbon dioxide. These values are given in Table 1 and range from a partial pressure of carbon dioxide of 0.91×10^{-3} to 51.35×10^{-3} atmospheres. The theoretical partial pressure of methane corresponding

to /

to equilibrium with a carbon saturated melt can be calculated as follows :

$$C + 2H_2 = CH_4 \qquad \Delta G^{\circ}_{1723} = 23,500 \text{ cal/mole} \quad (22)$$

$$K = \frac{pCH_4}{pH_2^2 \times a_c} = 1.04 \times 10^{-3}$$

Since the melt was saturated with carbon $a_c = 1$ and it can be assumed that $pH_2 = 1$

$\therefore pCH_4 = 1.04 \times 10^{-3}$ atmospheres

Since both the carbon dioxide and the methane molecules contain a single carbon atom, the partial pressure of methane should correspond to the partial pressure of carbon dioxide calculated from the experimental readings.

Thus, if equilibrium was reached between the hydrogen and the melt the partial pressure of carbon dioxide measured should also be 1.04×10^{-3}. It can be seen, therefore /

therefore, from Table 1 that on the whole the partial pressures of carbon dioxide measured in the runs using the mullite tubes were much higher than the theoretical value and also very erratic. In the case of the extremely high values obtained, for example in runs R3, R17, and R18, the only reasonable explanation would appear to be that the system was not vacuum tight and that considerable inleakage of air occurred resulting in the formation of large quantities of carbon monoxide. It is unlikely, however, that this was the case in all the runs giving high partial pressures of carbon dioxide. It was, therefore, obvious that the reason for these unsatisfactory, high and variable results must be investigated.

It is possible that some of the discrepancy may be attributed /

attributed to a reaction between hydrogen and silica in the mullite refractory resulting in the formation of silicon monoxide.

$$SiO_2 + H_2 = SiO + H_2O$$

The free energy of this reaction was calculated using current free energy data for the formation of SiO_2 [28], SiO [28, 29] and H_2O [22] giving a value of

$$\Delta G^{\circ}_{1700} = 50,990 \text{ cal/mole}$$

$$K = \frac{pSiO \times pH_2O}{pH_2 \times a_{SiO_2}} \qquad \log K = -6.55$$

$$K = 10^{-6.55}$$

pH_2 can be regarded as unity, and $pSiO \equiv pH_2O$

$$\therefore K = \frac{p^2H_2O}{a_{SiO_2}}$$

But a_{SiO_2} in mullite at 1450°C = 0.5 [30]

$$\therefore pH_2O = 0.38 \times 10^{-3} \text{ atmospheres.}$$

If it is assumed that all the water vapour reacts with carbon /

carbon in the iron, then $pH_2O \equiv pCO \equiv pCO_2$

$\therefore pCO_2 = 0.38 \times 10^{-3}$ atmospheres.

This value could have some significance in the results and it was decided to carry out a similar calculation on alumina to find if the problem of the formation of sub-oxides was relevant when using alumina tubes.

$$Al_2O_3 + 2H_2 = Al_2O + 2H_2O \quad \Delta G^{\circ}_{1700} = 128{,}000 \text{ cal/mole} \quad (22)$$

$$K = p^2H_2O \times pAl_2O$$

$$\log K = -16.5$$

$$pH_2O = 2pAl_2O$$

$$K = 4p^3Al_2O$$

$$pAl_2O = 6.3 \times 10^{-5}$$

Hence $pH_2O = 0.126 \times 10^{-3}$ atmospheres.

Thus it can be seen that the reduction of alumina by hydrogen is significantly less than the reduction of mullite and for that reason mullite was replaced by alumina. Having replaced the mullite tube and thermocouple sheaths /

TABLE II

Runs Performed at 1450°C in an Al_2O_3 Tube with C saturated Iron in an Al_2O_3 Crucible

Run No.	$P_{CO_2} \times 10^3$ (atmos)	Flow Rate (Ml/Min)	Count Rate on 4cm sample (counts/min)	Specific Activity (counts/Cm Hg)	Notes
P_1	7•02	60	7,800	1,950	A new tube was used.
Blanks	1•56	100	3,127	2,010	
	1•69	40	2,361	1,774	
	3•90	110	-	-	
	0•78	110	1,300	2,167	
	0•78	60	1,000	1,667	
	1•43	100	1,790	1,627	
	0•78	130	1,210	2,017	
P_2	3•90	40	6,800	2,266	
Blanks	1•17	50	2,500	2,778	
	0•91	70	1,950	2,785	
Run	7•41	140	9,150	2,288	
Blanks	3•25	40	5,800	2,320	
	1•3	40	-	-	On cooling the tube was leaking
P_3	0•26	60	662	3,310	A new tube was used
Blanks	1•04	50	2,150	2,688	
	0•65	140	1,390	2,780	
Run	2•99	120	4,920	2,139	
Blank	0•65	70	1,360	2,720	
Run	2•99	100	5,580	2,426	

sheaths by alumina refractories another series of experimental runs was carried out. The results of these runs P1, P2 and P3 are shown in Table 11. In each case the results shown were obtained consecutively by passing two litres of gas over the melt each time. As indicated in the table, the majority of these runs were blank runs in which inert gas was passed over the melt. The results obtained for the hydrogen runs were still high compared with the theoretical value. The most disturbing feature of the results, however, was the relatively high partial pressures of carbon dioxide recorded in the blank runs. It is obvious that the theoretical value for hydrogen runs is unlikely to be approached while appreciable quantities of carbon dioxide are formed during a blank run immediately preceeding the admission of hydrogen to the reaction chamber /

chamber. The fact that the specific activity of the carbon dioxide formed in the blank runs was comparable with that obtained in hydrogen runs, within the probable limits of accuracy of the pressure measurements, indicated that some reaction involving carbon from the melt was proceeding while inert gas was flowing through the reaction chamber. It therefore became necessary to find the source of, and if possible eliminate, these high blank values.

The possible sources considered for the high blanks were firstly crucible reaction, that is, reaction between the crucible material and carbon in the melt and, secondly, oxygen being introduced into the reaction chamber either from the gas stream or by leakage. These sources will result in the formation in the reaction chamber /

chamber of carbon monoxide which will in turn be converted to carbon dioxide on passing through the copper oxide furnace. The radioactive count does not indicate whether the carbon dioxide condensed, originated from methane or carbon monoxide, since both gases will result in the same amount of $C^{14}O_2$ being formed.

The most obvious source of the carbon monoxide would appear to be from the crucible reaction and this problem was therefore given considerable attention.

Reaction between the Crucible and the Melt

The choice of a suitable crucible material is rather limited in work of this kind since the material must be a high temperature refractory resistant to iron and carbon attack and also impermeable to liquid iron. The

normal /

normal type of crucible material used is a stable refractory metal oxide although a nitride or a sulphide could be used. From free energy data the oxides of the following metals would appear to be suitable: aluminium, beryllium, calcium, magnesium, thorium and zirconium. Reactions between these oxides and carbon in iron, with the subsequent formation of carbon monoxide, are possible by two mechanisms. These involve reductions of the oxide by carbon with the formation of (a) the metal or (b) the metal carbide. Both these reactions were considered from the thermodynamic point of view. (a) The reaction of the metal oxide with carbon can be considered as follows, taking alumina as an example:

$$Al_2O_3 + 3\underline{C} = 2\underline{Al} + 3CO \quad \Delta G^{\circ}_{1700} = 83,220 \text{ cal/mole} \quad (22)$$

for carbon saturated iron $a_c = 1$ $\therefore K = p^3CO \times a_{Al}{}^2$

For /

For the calculation, a_{Al} shall be assumed to be unity, that is, saturation of aluminium in the melt. During these experiments the activity of aluminium will not be unity and hence there will be a larger value for the partial pressure of carbon monoxide. However, in the calculation any alteration in the activity of aluminium will have a smaller relative effect on pCO since pCO appears to the third power in the expression whereas a_{Al} is only squared.

$$\text{Hence } \log K = -10.7$$
$$\therefore pCO^3 = 10^{-10.7}$$
$$pCO = 10^{-3.6}$$

This value representing the partial pressure of carbon monoxide required above the melt to suppress the reaction. The results obtained, by similar calculations, for all the above metal oxides have been tabulated below:

	Al_2O_3	BeO	CaO	MgO	ZrO_2
pCO	$10^{-3.6}$	$10^{-5.3}$	10^{-6}	$10^{-3.7}$	$10^{-3.9}$

(b) /

(b) The formation of a metal carbide must also be considered, and again alumina is used as an example.

$$2Al_2O_3 + 9\underline{C} = Al_4C_3 + 6CO \quad \Delta G^{\circ}_{1700} = 133,640 \text{ cal/mole} \quad (22)$$

$$K = pCO^6 \quad \text{for carbon saturation}$$

$$\log K = -17.2$$

$$pCO^6 = 10^{-17.2}$$

$$pCO = 10^{-2.9}$$

The results have again been tabulated below for the other metal oxide with the exception of beryllium oxide since a value for the free energy of formation of beryllium carbide could not be obtained.

	Al_2O_3	BeO	CaO	MgO	ZrO_2
pCO	$10^{-2.9}$	-	$10^{-2.8}$	10^{-6}	$10^{-1.4}$

It can be seen from these figures based on equilibrium data that all the oxides will react with carbon to some extent /

extent. The kinetics of these reactions will be the final limiting factor, but as the rate of the reactions in unknown the choice of the material used for the crucible must be made from the equilibrium data. Although some materials appear to be more suitable on considering one of these reactions, the advantage may not hold on considering the reactions together. Thus beryllium oxide, which would appear to be most satisfactory since there is little reduction of the oxide to the metal, would not be an immediate choice without data on the formation of beryllium carbide. When both reactions (a) and (b) are considered there is little to choose between the oxides although lime and magensia would appear to be slightly better than alumina.

The final choice of the crucible material, however /

however, cannot be based solely on thermodynamic date. Magnesium has a high vapour pressure and hence the crucible reaction would tent to proceed more rapidly due to the continued loss of magnesium into the gas phase. Lime crucibles are difficult to manufacture and store due to the rapid formation of calcium hydroxide on exposure to atmosphere. One apparently successful technique is to produce a solid block of calcium oxide by arc melting, the rate of hydration in this case being much lower, but this is an extremely difficult technique. Lime crucibles can be manufactured by other techniques but the physical properties of these crucibles cannot be guaranteed. Alumina, however, is available in a form which has superior physical properties and since it is not markedly inferior from the theoretical point of view it was, as has been stated previously, decided

to /

TABLE III

Blanks Performed at 1450°C in an Alumina Tube with C saturated Iron with up to 0·2% Al in an Alumina Crucible

Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Notes
P4	0·78	190	New tube.
	0·39	130	
	0·26	130	
	0·39	100	After 2 H_2 runs
P 6	0·91	100	New tube.
	0·52	120	
	0·26	180	After 2 H_2 runs
	0·65	140	After 2 H_2 runs.
P7	0·91	110	
	0·26	200	
P9	0·91	130	
P10	1·04	110	New Tube
P13	0·0	140	New tube
	0·91	120	After 2 H_2 runs
	0·78	120	
	1·04	160	
P14+	0·65	150	New tube
P16+	0·91	100	New tube
P18+	0·0	125	New tube
	0·0	133	
	0·78	200	After 11 H_2 runs

Runs marked with + indicate runs using a molybdenum furnace.

to use alumina crucibles in the preliminary runs at least.

If the blanks, which were obtained in runs P1 - P3, were due solely to crucible reaction it would indicate that the reaction was proceeding fairly rapidly. This would of course mean that alumina was not a satisfactory crucible material. In an attempt to reduce the extent of the crucible reaction, up to 0.2 per cent aluminium was added to the melt in runs P4 - P18 since this should tend to reduce the formation of aluminium by reduction of the oxide. The results of blank determinations carried out under these conditions are shown in Table 111. It can be seen from the results that the addition of aluminium to the melt did not affect the blank values greatly. However, the blank values showed two trends which were confirmed /

confirmed in later runs. Continued purging of the reaction chamber by inert gas resulted in a decrease in successive blank determinations and there was also a tendency for higher blank values to be obtained after a number of hydrogen runs had been carried out.

A further observation was made during this series of runs. It was noted that the end of the alumina gas-inlet tube which had been immersed in the melt appeared to have been attacked by the metal, and that a considerable amount of metal droplets had been splashed on to the reaction tube wall during the experiments. This led to a further consideration of the mechanism of the reactions, discussed above, between carbon in the melt and alumina. While the thermodynamics of these reactions are identical whether the crucible, gas-inlet tube /

tube or reaction tube is considered, the kinetics of the reaction are quire different. Around the immersed portion of the gas-inlet tube there is extreme agitation of the melt by the bubbling gas, with the result that any carbon monoxide formed from the reaction between the tube and the melt is immediately carried off in the gas stream and a fresh metal surface is continually presented to the tube. In the crucible reaction, however, there is less agitation of the bath at the melt crucible interface and the rate of reaction is diffusion controlled by either the rate of removal of carbon monoxide from, or the rate of migration of carbon to, the interface. Thus any reaction between the melt and alumina will be more rapid at the gas-inlet tube than at the crucible wall. The rate of reaction between metal beads and the tube wall will also be diffusion controlled but as the metal beads have a large surface

to /

to volume ratio removal of carbon monoxide to the gas phase will be much quicker than in the crucible, hence the rate of reaction between the metal beads and the tube wall will also be faster than the crucible reaction.

In order to eliminate attack of the gas-inlet tube and to reduce the danger of metal splashing on to the tube wall, the gas-inlet tube was raised to a position slightly above the metal surface so that the gas stream was impinging on to the surface. This should still give intimate contact between the gas and metal and allow rapid attainment of equilibrium. This procedure was adopted in run P18 and in subsequent experiments and resulted in a significant decrease in the blank values, the partial pressure of carbon dioxide produced by two litres of inert gas being in many cases too small to measure /

TABLE IV

Runs Performed at 1450°C in a Molybdenum Furnace with C Saturated Iron in an Al_2O_3 Crucible with an Al_2O_3 Tube

Run No.	$P_{CO_2} \times 10^3$ (Atmos)	Flow Rate (ml/min)	Notes
P14 Blank	0.65	150	New tube
Run	6.24	140	
P15	4.42	130	
Runs	3.90	very slow	
	1.56	200	
	4.29	170	
	3.38	150	
	2.99	140	
P16 Blank	0.91	100	New tube
Runs	4.55	80	
	2.99	90	
	2.34	180	
	3.12	200	
	5.20	very slow	
	2.08	210	
	4.42	120	
P17	4.94	100	
Runs	4.42	181	
	6.63	133	
	6.11	133	
	6.50	154	
	7.8	93	
	6.11	181	
	5.2	190	
	10.4	very slow	
	6.11	222	
	6.11	167	
	6.63	98	
Blanks	0.91	167	
	0.91	125	Tube leaking

(cont'd)

TABLE IV (Cont'd)

Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Notes
P18 Blanks	0·0	125	New tube
	0·0	133	
	1·43	200	
	5·07	89	
Runs	1·56	190	
	3·25	200	
	4·16	95	
	4·81	133	
	4·16	236	
	5·59	89	
	1·82	211	
	4·81	182	
	3·64	160	
Blank	0·78	200	
P19 Blank	0·78	83	New tube used prior to this run for H_2/H_2O study
	0·52	111	
	0·52	133	
	0·0	133	
	0·13	118	
Runs	4·81	95	
	2·21	286	
	4·55	111	
	2·60	286	
	5·20	67	
P20	0·65	154	New Tube
	0·13	154	
Blanks	0·00	118	
	2·08	233	
	1·69	333	
	3·64	57	
Runs	1·82	222	
	2·34	118	
	2·73	77	

measure. The fact that this procedure was effective, whereas aluminium additions to the melt were not, may indicate that the quantity of aluminium added was insufficient to alter the equilibrium appreciably.

It now appeared that the source of the high blank values had been traced and eliminated. In subsequent experiments for example P19 and P20 (Table 1V), it was found that very low blank values could be obtained by purging the reaction tube for a short time with inert gas. This presumably had the effect of removing any traces of absorbed oxygen from the reaction chamber. On this basis the original choice and the continued use of alumina crucibles was justified since the extent of the crucible reaction during the course of a single run appeared to be negligible.

Results /

Results obtained in the Hydrogen Runs

While endeavouring to reduce the blanks, hydrogen runs were continued. It was found that the results in all cases were very much higher than the theoretical partial pressure of methane of 1.04×10^{-3} atmospheres, even when the blank value was taken into account (Table 111). This was still found to be the case after the blank had been reduced to negligible proportions. Another feature of the results was that they showed considerable variation from run to run (Table 1V). The reason for these high results was unknown but various possibilities were considered.

As an initial step in trying to explain why the results of the hydrogen runs were higher than the predicted /

predicted theoretical value, the source of the thermodynamic data, from which this value was calculated, was checked. The data [22] which had been used were found to be based on accurate calorimetric measurements by the National Bureau of Standards [31] which is an authoritative source. The accuracy of the free energy of formation of methane, however, was given to ± 500 cal/mole so as an additional check it was decided to find the effect of such a variation on the predicted partial pressures of carbon dioxide and also to find the effect of an appreciable variation in temperature (± 23°C) from 1450°C. The results are tabulated below.

	ΔG°_{1723}	ΔG°_{1723} +500 cal	ΔG°_{1723} -500 cal	ΔG°_{1700}	ΔG°_{1746}
ΔG° Values (cal/mole)	23,523	24,023	23,023	22,920	24,125
$pCO_2 \times 10^3$	1,035	0.895	1,20	1.13	0.953

Thus it can be seen that making allowance for the maximum /

maximum error in the thermodynamic data and for relatively large variations in temperature has no appreciable effect on the resultant partial pressure of carbon dioxide and could certainly not explain the order of difference obtained between the experimental and the theoretical results.

The possibility of hydrogen reacting with carbon to form hydrocarbons other than methane was also considered, since any other hydrocarbons formed would result in additional carbon dioxide and hence higher pressures would be obtained experimentally. Formation of highly complex hydrocarbons would be unlikely but the simpler hydrocarbons, acetylene, ethylene and ethane may be formed. The resultant carbon dioxide formed due to these gases being produced was calculated

using /

using the appropriate thermodynamic data [22,32] as follows. Formation of acetylene:-

$$2\underline{C} + H_2 = C_2H_2 \qquad \Delta G^{\circ}_{1700} = 31{,}990 \text{ cal/mole}$$

$$K = pC_2H_2 \qquad \text{since } a_c = 1 \text{ and } pH_2 = 1$$

$$\log K = -4.1$$

$$\therefore \quad pC_2H_2 = 0.95 \times 10^{-4} \text{ atmospheres}$$

$$\text{hence } pCO_2 = 0.19 \times 10^{-3} \text{ atmospheres}$$

Similar calculations were carried out for the formation of ethylene and ethane and values of 0.089×10^{-3} and 0.615×10^{-7} atmospheres partial pressure of carbon dioxide were obtained respectively. Thus it would appear that the more complex the hydrocarbon molecule the less likelihood there is of it forming and there is no necessity to consider longer chain hydrocarbons. From these results it can be seen that these reactions could only contribute up to 0.28×10^{-3} atmospheres to the experimental results still leaving the major

part /

part of the discrepancy unexplained.

Purity of Gases Entering the Reaction Chamber

The presence of water vapour in the gases entering the reaction chamber is a possible source of high experimental results, since this would lead to the formation of carbon monoxide by the reaction :-

$$H_2O + \underline{C} = H_2 + CO$$

Carbon monoxide may also be formed indirectly by oxidation of methane,

$$CH_4 + H_2O = CO + 3H_2$$

This second reaction leads to the formation of carbon monoxide at the expense of methane and might therefore result in a low methane content. It was of course impossible at this stage in the investigation to tell whether or not oxidation of methane was occurring.

In /

In view of the importance of excluding water vapour, precautions had been taken, as described earlier, to dry the gases entering the furnace by passing over magnesium perchlorate $Mg(ClO_4)_2$. The partial pressure of water vapour should be reduced by this desiccant to 1.24×10^{-7} atmospheres (34) eliminating the possibility of high results from this source. There is however the danger that magnesium perchlorate will be hydrated to form $Mg(ClO_4)_2\ 3H_2O$ resulting in a higher water vapour pressure in the system. For this reason a molecular sieve material (Type 5A) was used as a drying agent in later runs, from P29 onwards. This, however, did not have any obvious effect on the results.

Before dismissing the question of water vapour in the system consideration was given to a further possible /

possible reaction. Turkdogan et al [6] have suggested that at low water vapour pressures the following reaction may occur.

$$3CH_4 + 2Al_2O_3 = Al_4C_3 + 6H_2O \quad \Delta G^{\circ}_{1700} = 220,640 \text{ cal/mole} \quad (22)$$

Assuming that the partial pressure of methane corresponds to equilibrium with hydrogen and carbon, this would result in a partial pressure of water vapour equal to 0.574×10^{-6} atmospheres.

If the water vapour formed was continuously converted to carbon monoxide by reaction with carbon in the melt in a cyclic process, such as used by Turkdogan et al [6], this reaction could result in appreciable formation of carbon monoxide. In the present study, however, the gases were not cycled and the water vapour pressure of the dried hydrogen (0.124×10^{-6} atmospheres) was /

was very close to the equilibrium value of 0.574 x 10^{-6} for the above reaction. Thus any contribution of carbon monoxide from this source would be negligible in the present work.

The possibility of hydrogen carrying other impurities such as oxygen or hydrocarbons into the reaction chamber was now considered. The presence of oxygen, like water vapour, would lead to a high result since it would react with either the methane or the carbon in the melt to form carbon monoxide.

$$\underline{C} + \tfrac{1}{2}O_2 = CO$$

In order to test the purity of the hydrogen the following simple experiment was performed. Five litres of hydrogen was passed through the empty furnace tube at 1450°C and any water formed, due to the reaction of any oxygen /

TABLE V.

Results of the Hydrogen-Water Vapour Experiments where H_2 was passed through the empty tube at 1450°C and the amount of water formed was measured.

Position of run	$P_{H_2O} \times 10^3$ (atmos)	Preceding value of H_2 run	Subsequent value of H_2 run	Notes
Between P10 P11	1·64	3·9	3·38	Tube leaking
P17 P18	0·39	6·63	-	
P18 P19	0·18	-	3·10	New tube used
P20 P21	0·43	2·73	4·32	

oxygen present with the hydrogen, was measured by passing the gas through a midvale bulb containing magnesium perchlorate. It should be noted that this experiment does not measure simply the oxygen carried into the furnace chamber but also the oxygen present from other sources, tube leaks, occluded oxygen and the reaction between the hydrogen and the alumina. The results from these experiments are shown in Table V from which it can be seen that the results vary from 0.18×10^{-3} to 1.64×10^{-3} atmospheres partial pressure of water vapour. It should be noted that the low value was obtained with a new tube while the high value was obtained with a tube which was thought to be leaking. While these results would represent an appreciable contribution to the carbon dioxide pressures obtained in presence of a melt even the highest value does not account for the

level /

level of the result obtained in a subsequent hydrogen - methane run performed in the same tube (see Table V). Since these results are obviously relevant to a satisfactory explanation of the high carbon dioxide pressures, they are discussed in greater detail at a later stage.

While considering oxygen and water vapour being transported into the reaction chamber by hydrogen, the possibility of any hydrocarbons being present in the hydrogen was considered. Any hydrocarbons introduced into the reaction chamber by hydrogen would produce carbon dioxide on passing through the copper oxide furnace. To find, if in fact hydrogen did contain an appreciable amount of hydrocarbons, the hydrogen was passed directly through the copper oxide furnace and any carbon dioxide formed was frozen out. The amount

of /

of carbon dioxide formed was negligible, such a mechanism therefore was rejected.

Danger of Tube Leaking

It had been found that the alumina tubes after one or two runs with hydrogen were no longer vacuum tight and in some cases slight pin hole porosity could be detected in the region of the tube corresponding to the hot zone of the furnace. If the tubes were not vacuum tight there was the danger that oxygen would diffuse into the reaction chamber and react with the melt. In an attempt to eliminate any danger of oxygen diffusing into the furnace tube it was decided to use a molybdenum wound furnace in place of the crucible furnace previously employed. The purpose of this was to obtain an arrangement in which the atmosphere surrounding the reaction tube was cracked /

cracked ammonia. Thus, in the event of the tube leaking the gases entering the reaction chamber should not contain oxygen and should not contribute to high carbon dioxide pressures. The results of these runs are shown in Table IV but there is no marked difference in the amount of carbon dioxide formed as compared to previous results in the crusilite furnace. This appeared to discount the view that leaking of the furnace tube could be a major source of oxygen.

At this stage in the investigation it appeared that all the obvious reasons for the high carbon dioxide pressures in the experimental runs had been considered. None of the mechanisms so far discussed could be responsible for the level of the results obtained. It will be noted that the source of error in most of the above hypothesis

was /

was the formation of carbon monoxide. However, no direct proof of the presence of this gas in the reaction chamber had been obtained, since as mentioned previously the radioactive technique was capable of measuring only the total amount of carbonaceous gas formed and gave no indication of the constituent gases present. If further progress was to be made in ascertaining the exact mechanism responsible for the failure to reduce the level of the experimental results to that corresponding to the theoretical value for the hydrogen - methane equilibrium, it was felt that an analytical technique would be required which was capable of giving at least a qualitative analysis of the furnace gases.

It was for this reason that the gas chromatography apparatus was constructed. This proved to be an extremely /

TABLE VI

Runs Performed at 1450°C with an Al_2O_3 Tube in an Alumina Crucible
Gas Chromatography Results being given

Run No.	$P_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Chromatography $P_{CH_4} \times 10^3$	Chromatography $P_{CO} \times 10^3$	Notes
P23 Blanks	0·39	72			
	0·13	118			
Runs	1·56	105			
	1·17	182	0·3	0·8	
	1·04	167			
	1·3	200			
	1·43	143			
	1·17	167			
	2·21	74			
	2·34	77			
P31 Blanks	0·78	100			
	0·13	100			
	0·13	111			
Runs	4·29	117	0·2	2·0	
	1·43	117	-	-	
	2·08	117	0·4	2·5	
	2·08	125	-	-	
	2·08	-			

extremely useful piece of equipment, since it was possible, not only to identify positively both carbon monoxide and methane, but also to obtain an estimate of the relative quantities in which these gases were present. However, due to the difficulty in measuring the very small areas under the peaks and the inaccuracy in sampling from the palladium thimble, it could not be claimed that the results obtained by the gas chromatography technique were of sufficient accuracy to allow carbon activity values to be derived.

The results of the runs in which the gas chromatography apparatus was used to analyse the gases present are shown in Table VI. From this table it can be seen that in all these runs carbon monoxide was present, the quantity usually accounting for the bulk of /

of the carbonaceous gas. It was also shown that the percentage of methane present was less than the equilibrium value of 1.04×10^{-3} atmospheres. This may be explained on the basis that the formation of carbon monoxide indicates the presence of some oxygen source in the reaction chamber. This might also be expected to reduce the amount of methane by the following reaction :

$$CH_4 + \text{"O"} = CO + 2H_2$$

Since oxidation of methane appears to take place, it follows that even if very accurate methane analysis was obtained, any carbon activity values determined under these conditions would be liable to serious error. Having confirmed that some source of oxygen is present in the reaction chamber, it was decided, with the use of the gas chromatography apparatus, to make more stringent efforts /

efforts to determine the source. The possibilities are as has been stated earlier, crucible reaction, tube leaking or oxygen impurities in the gas stream. In order to determine which of these mechanisms was the most likely source of oxygen the following experiments and experimental determinations were carried out. (a) The effect of different crucible materials, (b) the effect of temperature and composition of the melt, (c) the relationship between flow rate and the pressure of carbon dioxide formed, and (d) the relationship between tube life and the pressure of carbon dioxide formed.

(a) The Effect of Different Crucible Materials on the Results

Although the attainment of a low blank value had previously been accepted as evidence that the extent of crucible /

TABLE VII

Results of Runs using a Be O Crucible in a Molybdenum Furnace

Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Notes
P21 Blanks	1·82	117	
	1·04	125	
	1·56	77	
	1·04	100	
	0·52	125	
	0·78	125	
	2·08	64	
Runs	8·19	117	
	2·73	133	

Results of Runs using a B.N. Crucible in a Crusilite Furnace

Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Chromatography $p_{CH_4} \times 10^3$	Chromatography $p_{CO} \times 10^3$	Notes
P24 Blank	1·82	83			Only 10gm of metal in a small crucible
	0·13	100			
	0·13	100			
	0·0				
	3·64	167			
Run	2·6	200	0·2	2·0	
	1·17	95	0·3	4·0	
	1·56	100			

(Cont'd)

TABLE VII (Cont'd)

Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Chromatography $p_{CH_4} \times 10^3$	Chromatography $p_{CO} \times 10^3$	Notes
P25 Blank	1·95	80			New tube
	0·13	100			
	1·82	117			Only 10 gm of metal in a small crucible
	1·30	100			
	2·08	117			
	1·04	250			
Run	1·04	173	0·4	2·0	
	0·91	154			
	1·30	84			
	1·69	72			
	1·43	80			
P26 Blank	1·04	117			50 gm sample
	0·52	62			
	0·00	117			
	0·13	-			
	5·72	133			
	6·24	133			
Run	8·84	143	0·6	5·0	
	6·11	117	0·5	5·0	

crucible reaction was negligible in the presence of an inert gas, there is a remote possibility that the reaction may be accelerated by the presence of hydrogen. It was considered therefore that the use of different crucible materials might affect the experimental results.

The alumina crucible was replaced in the first instance by a beryllia crucible since it appeared more favourable on considering the thermodynamic data for the reduction of the oxide to beryllium by carbon, as has been shown earlier. The beryllia crucible which was produced commercially, was well shaped but did not appear to be as well fired as the alumina crucibles, having a more porous appearance. As can be seen from Table V11 the partial pressure of carbon dioxide measured in this experiment was very high, so that it was still not known /

known whether crucible reaction was a source of oxygen or not. If the crucible is reacting with the melt to form carbon monoxide this difficulty could be overcome by using an oxygen-free crucible. For this reason it was decided to use boron nitride as the crucible material. The boron nitride was available in the form of a cylindrical rod and it was machined into a suitable shape for a crucible. The results of the runs using such a crucible are also shown in Table VII from which it can be seen that, although the results are low in P25, they are not markedly better than in some of the runs using an alumina crucible. The gas chromatography results show that carbon monoxide is still produced which indicates that oxygen is still present in the system even when the crucible is oxygen-free. These results therefore finally eliminated crucible reaction as the primary /

primary source of oxygen.

(b) The Effect of Composition of the Melt and Temperature on the Results

If the source of carbon monoxide is due to an equilibrium reaction with the melt, lowering the percentage of carbon in the melt, will reduce the carbon activity and hence less carbon monoxide will be formed. On the other hand if the reaction producing carbon monoxide has not reached equilibrium a lower value of carbon activity will not necessarily lower the amount of carbon monoxide formed. Thus if runs are carried out with a lower carbon concentration the amount of carbon monoxide formed will indicate whether the reaction producing carbon monoxide has reached equilibrium or not.

The results of the runs where the carbon concentration

was /

TABLE VIII

Runs Performed at 1450°C in an Alumina Tube with 2·51% C in Iron in an Alumina Crucible

Run No.	$P_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Chromatography $P_{CH_4} \times 10^3$	Chromatography $P_{CO} \times 10^3$	Notes
P30	0·78	286			New tube
	1·56	80			
Runs	0·65	80			
	0·65	166			
	0·65	111			
P32	1·3	64			
Blanks	0·26	91			
	0·00	125			
	4·69	95			
	1·17	165	nil	1·0	
	2·34	125	nil	1·0	
	2·08	125	-		
Runs	1·17	250			
	2·08	143	nil	2·0	
	1·3	250			
	4·94	70			

TABLE VIII (Cont'd)

Runs Performed at 1350°C in an Alumina Tube with C saturated Iron in an Al_2O_3 Crucible

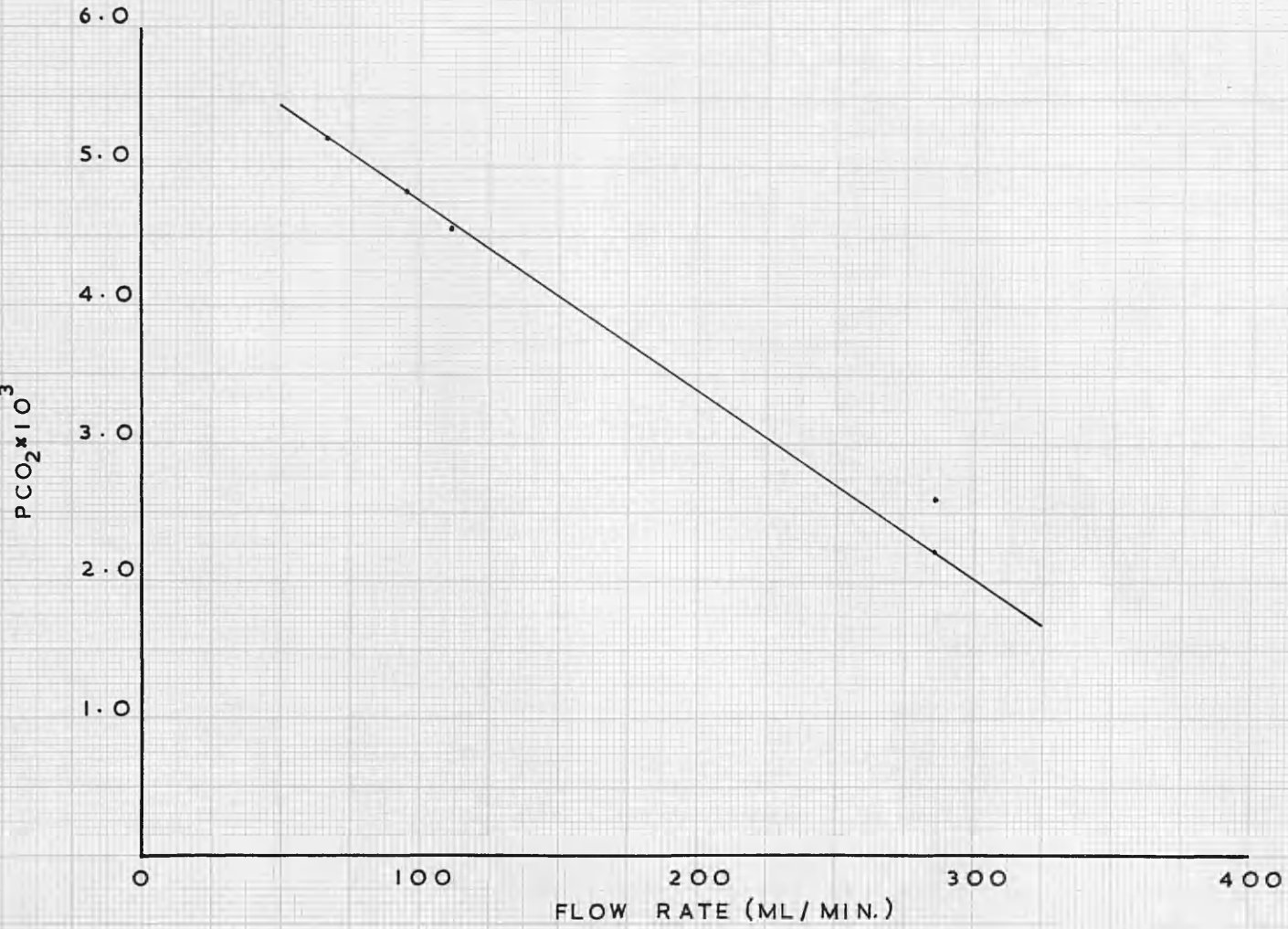
Run No.	$p_{CO_2} \times 10^3$ (atmos)	Flow Rate (ml/min)	Chromatography $p_{CH_4} \times 10^3$	Chromatography $p_{CO} \times 10^3$	Notes
P33 Blanks	0·13	100			New tube
	0·13	111			
	0·00	117			
Runs	1·04	87	0·3	0·4	
	0·65	182			
	0·13	222			
	0·52	87			
	0·65	105			
	0·52	133			

was lowered to half the saturation value are shown in Table VIII. In P30 the pressure measured was extremely low but unfortunately a sample was not taken for gas chromatography. In P32 the pressure measurement was not quite as low but the sample taken contained such a small quantity of methane that it could not be measured by the gas chromatography technique. The amount of carbon dioxide, however, appeared to be similar to that obtained with carbon saturated melts.

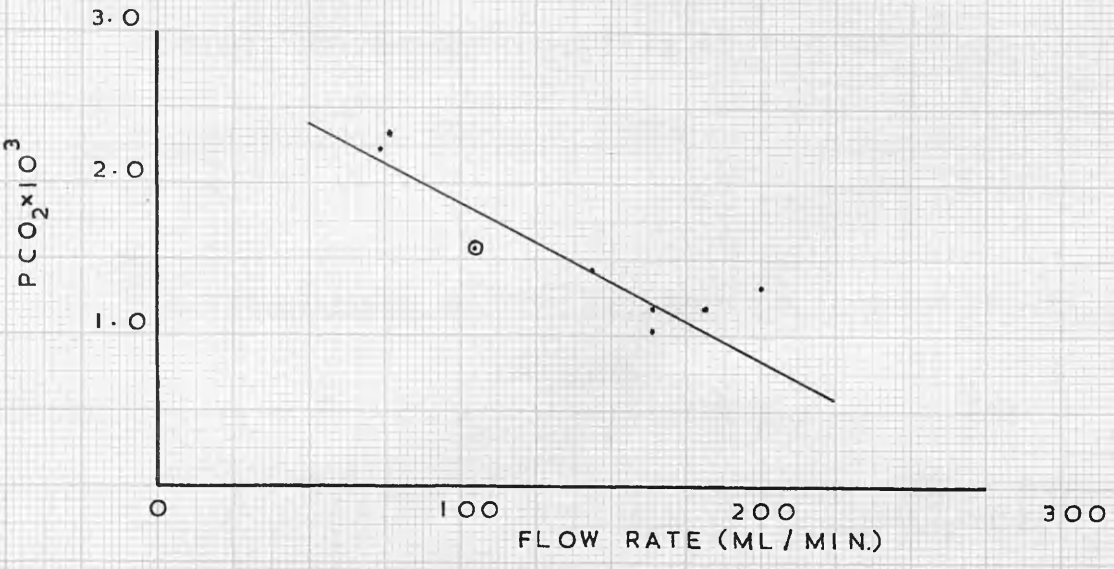
The low value of methane was to be expected since reducing the carbon concentration by half will reduce the amount of methane formed in the hydrogen-methane equilibrium. The fact that the percentage of carbon monoxide was the same as in the carbon saturated melts indicates that the reaction resulting in the formation of carbon monoxide has not reached equilibrium.

The /

The results of the run carried out at 1350°C is shown also in Table VIII. From this result it can be seen that the partial pressure of carbon dioxide was approximately 0.55×10^{-3} atmospheres, a very low value indeed. The amount of carbon dioxide measured in the gas chromatography apparatus was also very low, however, the methane value was similar to the value obtained with carbon saturated melts at 1450°C. If equilibrium was reached in the hydrogen - methane reaction the percentage of methane should be higher at 1350°C than at 1450°C since methane becomes less stable with increasing temperature. The low value of carbon monoxide further confirms that the source of oxygen is not impurities in the gas stream, since the quantity of oxygen or water vapour introduced is independant of the temperature of the reaction chamber and the rate of reaction of these impurities with the melt will /

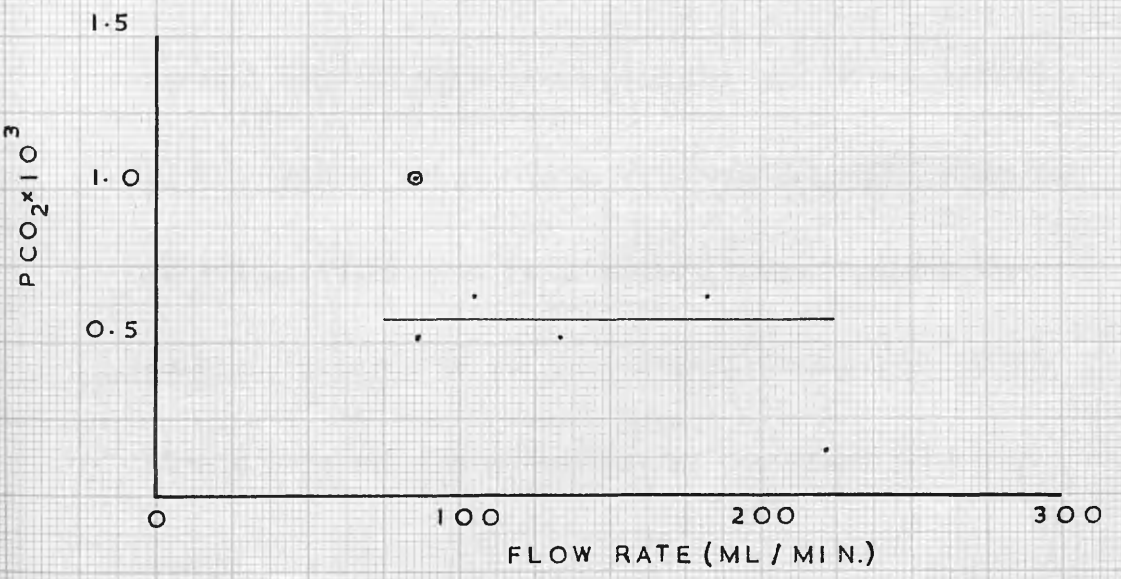


GRAPH VIII RELATIONSHIP BETWEEN FLOW RATE AND PCO_2 IN RUN P_{19}



GRAPH IX RELATIONSHIP BETWEEN FLOW RATE AND PCO_2 IN RUN P_{23}

⊙ INDICATES FIRST RUN



GRAPH X RELATIONSHIP BETWEEN FLOW RATE AND PCO_2 IN RUN P_{33}

will not be markedly affected by the drop in temperature from 1450°C to 1350°C.

(c) Relationship between Flow Rate and Pressure of Carbon Dioxide

The flow rate of hydrogen through the reaction chamber was measured in all the runs. It might be expected that this variable would have some effect on the experimental results. In order to show whether or not this was the case values of flow rate against the partial pressure of carbon dioxide produced was plotted for several runs in Graphs VIII-X. These graphs are typical of the type of relationship obtained and while they show considerable scatter it is possible to interpret the results in terms of the best straight line through the points. It will be noted that in the graph for P19,

in /

in which high partial pressures of carbon dioxide were obtained that there is a definite trend indicating a marked degree of flow rate dependence. This trend is less marked in P23, in which the partial pressures of carbon dioxide were lower and in run P33 where still lower partial pressures of carbon dioxide were recorded there appears to be little or no flow rate dependence.

The flow rate dependence of the results might at first appear to be due to equilibrium not being attained in the hydrogen - methane reactions at increased flow rates. However, on considering the results of runs P23 and P33 it can be shown that this is not in fact the case. The results of the gas chromatography analysis on P33, which is not flow rate dependent, indicate that the amount of methane present is similar to that in P23 which is flow rate dependent. The difference

between /

between these two series is the amount of carbon monoxide present, there being an appreciable quantity in P23 whereas there is little or no carbon monoxide in P33. Thus it follows that the flow rate dependence of P23 is due to the variation in the amount of carbon monoxide formed and not the hydrogen - methane equilibrium.

If carbon monoxide was produced from oxygen or water vapour, introduced by the hydrogen, the quantity formed would not be expected to depend on flow rate, since the rate of reaction of these impurities with carbon in the melt would be rapid. This adds further confirmation to the view that impurities in the gas stream are not the source of oxygen in the reaction chamber.

The evidence therefore leads to the conclusion that the supply of oxygen to the reaction chamber is

time /

time dependent, thus in a run at a fast flow rate only a small quantity of oxygen is available and consequently a low partial pressure of carbon monoxide is formed, whereas the converse is true at low flow rates. Since crucible reaction has been dismissed as a source of oxygen the only possible explanation would appear to be the slow permeation of oxygen through the tube wall. This would of course be a slow, time dependent process and would account for the type of flow rate dependence observed in the experimental results. Further consideration was therefore given to the behaviour of the alumina reaction tubes used in the experiments.

(d) <u>The Relationship between tube life and the partial pressure of carbon dioxide formed</u>

Having dismissed all other possibilities for the source /

source of oxygen it was felt that a detailed examination of the results was necessary to find if the tube could possibly be the source of oxygen.

On studying the results in Tables II -VIII it is apparent that a new tube was required for every second or third series of runs, the tube being replaced when it was shown to be leaking. In fact in a few of the tubes there was evidence, after a number of runs, of very slight porosity. When the results are studied with reference to the blanks and the runs using hydrogen it can be seen that low blanks do not always result in low values in the hydrogen runs. On the other hand high blanks always result in high values in the hydrogen runs. It was also found in some instances, for example P13 and P18, that low blanks could be obtained initially but /

but the blanks obtained after subsequent hydrogen runs were considerably higher. The results of hydrogen runs were also generally higher on using the same tube for a further series of runs even although the tube appeared to be vacuum tight at the beginning of the series. There therefore appeared to be a distinct relationship between the length of time a tube was used and the level of the results obtained. A detailed consideration of the behaviour of alumina tubes in the present investigation is developed in the following section.

Behaviour of Alumina Tubes during Experimental Investigation

From the experiments which have been described it was concluded that the only possible source of oxygen, leading to the observed formation of carbon monoxide, was /

was the permeation of oxygen into the reaction chamber through the wall of the alumina refractory tube. This at first appeared to be a surprising conclusion since tubes were always tested before commencing a series of experiments and discarded when any appreciable leakage occurred, even although no actual porosity could be detected in the tubes.

The experimental results, however, indicated that oxygen was entering the system even in the absence of tube porosity and it was, therefore, concluded that solid state diffusion of oxygen through the tube wall must be occurring, presumably due to an oxygen pressure gradient between the outer and inner faces of the tube, due to a low oxygen partial pressure being established within the tube in presence of a reducing atmosphere. It

is /

is also probable that a solid state diffusion mechanism resulting in oxygen transfer across the tube wall would gradually lead to the development of micro-porosity in the refractory and eventually to pinhole porosity of the type found in some of the discarded tubes.

It was now considered whether a diffusion mechanism of the type postulated would allow satisfactory explanations to be obtained for the observed variations in the experimental results under varying conditions.

The observed pattern of low blank values, followed by relatively high partial pressures of carbon monoxide during hydrogen runs followed by higher blank values and still higher results in subsequent hydrogen runs using the same tube, is readily explained by such a diffusion /

diffusion mechanism. In the hydrogen runs a very low partial pressure of oxygen is established at the inner face of the tube wall. There is therefore a concentration gradient across the wall producing a net flow of oxygen to the reaction chamber. In the presence of an inert gas, however, no oxygen deficiency is produced at the inner face and the diffusion mechanism will be suppressed. This accounts for the low initial blanks obtained in a new tube.

After a series of hydrogen runs where diffusion has been taking place continuously micro-porosity will be developing in the tube wall and on carrying out a further series of blanks the results will be higher due to oxygen diffusing through the micro-pores rather than by solid state diffusion. It is also apparent that after /

after one series of hydrogen runs a further series in the same tube will result in higher partial pressures of carbon monoxide since solid state diffusion will be augmented by the micro-porosity produced during the first series of runs with a subsequent increase in the diffusion rate.

The flow rate dependence of the experimental results also agrees well with a mechanism of this type. The rate of oxygen supply will be diffusion controlled and hence time dependent. Since all the experimental results are based on passing a fixed volume of gas through the reaction chamber, the faster the flow rate the less time taken and hence the smaller the quantity of oxygen diffusing into the furnace gases. It also follows that the experiments in which little carbon monoxide /

monoxide was produced, that is, in which diffusion was very slow should show little flow rate dependence, as has been confirmed experimentally.

The run at 1350°C also substantiates this theory. The partial pressure of carbon monoxide measured was much lower than at 1450°C since at a lower temperature the diffusion rate will be lower. At lower temperatures the tube life would also be expected to increase since the rate of development of micro-porosity will be decreased.

The fact that in some series of runs low results could be obtained does not detract from the theory since on examining the tubes as obtained from the manufacturer it was apparent that each tube had different characteristics, for example, different wall thickness, and apparent differences /

differences in texture etc., in fact it was found in one instance that the tube was not even vacuum tight on arrival at the laboratory. Thus different tubes will have different initial diffusion rates and consequently the length of time to develop micro-porosity, will vary from tube to tube. The validity of the results may be accounted for by such changes in tube characteristics. Unfortunately it is impracticable to test the tube prior to use in the hydrogen - methane experiments since such a test would require an oxygen gradient to be established across the tube wall at 1450°C in order to measure the diffusion rate. After such a test the characteristics of the tube will have changed and micro-porosity might have formed while testing. Thus the conditions required to test the tube are in effect these responsible for deterioration in the tube. It also follows that

variation /

variation between tubes cannot be eliminated by performing a large number of experiments in a single tube, since deterioration is progressive throughout the tube life.

Thus the diffusion mechanism is capable of explaining a considerable number of the experimental observations. The apparent anomalies to this theory are the runs carried out in the molybdenum furnace and the results of the runs in which hydrogen was passed through the empty furnace tube, the quantity of water formed being estimated (referred to subsequently as hydrogen - water runs). In the molybdenum runs, since there is effectively a hydrogen atmosphere outside the furnace tube as well as inside, it might appear that diffusion of oxygen should cease because of the lack of an oxygen gradient.

The /

The experimental results, however, were still high in the molybdenum furnace. In the hydrogen - water runs where hydrogen is passing through the empty tube, the results indicate that lower partial pressures of water vapour are formed than when the melt is present. Again it might be thought that the same atmosphere is present in each of these cases and hence the diffusion rates should be similar and the same oxygen partial pressures should result. Both these apparent discrepancies can be explained when the partial pressure of oxygen in the reaction chamber is considered, since the partial pressure of oxygen is controlled not by the hydrogen atmosphere but by the carbon potential of the furnace gases which are in equilibrium with the carbon saturated melt. A suitable means of comparison is obtained if the reduction

of /

of alumina to its suboxide is considered as follows :

$$Al_2O_3 + 2H_2 = Al_2O + 2H_2O \quad \ldots (3)$$

$$\Delta G^{\circ}_{1700} = 128{,}100 \text{ cal/mole} \quad (22)$$

Hence by the calculation given previously

$pH_2O = 0.126 \times 10^{-3}$ atmospheres and from the equilibrium

$H_2O = H_2 + \frac{1}{2}O_2 \quad pO_2 = 1.21 \times 10^{-17}$ atmospheres.

$$Al_2O_3 + 2CH_4 = Al_2O + 2CO + 4H_2 \quad \ldots (4)$$

$$\Delta G^{\circ}_{1700} = 30{,}340 \text{ cal/mole} \quad (22)$$

$$K = 10^{-3.9}$$

$$K = \frac{p^2CO}{p^2CH_4}$$

$$\therefore \frac{pCO}{pCH_4} = 10^{-1.95}$$

At methane equilibrium $pCH_4 = 1.04 \times 10^{-3}$

$\therefore pCO = 1.04 \times 10^{-4.95}$ and from the

equilibrium, $CO = C + \frac{1}{2}O_2$, $pO_2 = 1.24 \times 10^{-22}$

It can be seen from these results that when the

carbon /

carbon saturated melt is present in the reaction chamber and partial pressure of oxygen in the system is much lower than when hydrogen is passed through the empty tube with the result that the oxygen gradient across the tube wall is increased and consequently the rate of diffusion of oxygen into the reaction chamber is much greater. For this reason the hydrogen - water experiments do not give an accurate measure of the amount of oxygen which will be present during a hydrogen run. However, the hydrogen - water results themselves are consistent with the diffusion mechanism since low results were obtained in a new tube and the highest result in a tube subsequently shown to be leaking.

The reason why the results of the hydrogen results are not lower in the molybdenum furnace also becomes obvious /

obvious on considering reactions (3) and (4). Even if the atmosphere surrounding the furnace tube was pure hydrogen the oxygen potential within the tube would be lower than that outside since the gas inside the furnace is in equilibrium with carbon, hence diffusion can still occur. In fact the partial pressure of oxygen will be higher than that corresponding to pure hydrogen, since the molybdenum furnace shell is not entirely gas tight, so that oxygen may diffuse into the chamber, and since the porous insulating material within the shell will tend to retain moisture.

There appears, therefore, to be excellent agreement between the experimental evidence and the proposed theory of diffusion transfer of oxygen to the reaction chamber under a sufficiently high oxygen gradient across

the /

the tube wall.

This theory of diffusion of oxygen through the alumina tube wall receives support from a recent study by Hayes, Budworth and Roberts [33], in which the permeability of dense sintered alumina to oxygen, nitrogen and argon was investigated in the region of 1700°C. In their experiments an alumina tube was evacuated at the test temperature surrounded by oxygen, nitrogen or argon at one atmosphere pressure. The rate of increase in pressure in the tube gave a measure of the permeability of the alumina to the gas. By this technique it was shown that oxygen could permeate through the alumina tube. Slight permeation of nitrogen was reported but none was detected in the case of argon. Another observation agreeing with the present study was that different tubes showed

different /

different tubes showed different rates of permeation. Hayes et al [33] stated however that in their investigation no permeation of oxygen was detected below 1500°C. This, at first sight, appears to conflict with the view that a similar mechanism is responsible for the results obtained in the present study 1450°C. This apparent anomaly can be explained, however, when the oxygen partial pressures in the respective systems are considered. In the experimental procedure of Hayes et al [33] the alumina tube was under vacuum. The actual pressure in the system is not stated but it is extremely unlikely that the oxygen partial pressure was reduced to 10^{-10} atmospheres, whereas in the present study, as has already been shown, the partial pressure of oxygen was about 10^{-22} atmospheres. Thus in the present study the oxygen gradient across the tube wall

was /

was much greater than in their work, and it is probable that, as a result, appreciable permeation could occur at 14500°C. It has been shown, in fact, in the present investigation that permeation was negligible when the tube was filled with inert gas, a condition corresponding to oxygen partial pressures of the order obtained by evacuation.

The actual mechanism by which permeation of oxygen occurs may depend on a degree of non-stoichiometry in the alumina. This is due to a low partial pressure of oxygen at the inside of the tube wall resulting in metal-rich non-stoichiometry because of oxygen vacancies, whereas at the outside wall there is oxygen-rich non-stoichiometry due to interstitial oxygen atoms. Thus an oxygen gradient is set up across the tube wall resulting /

resulting in a net diffusion of oxygen to the inside of the tube, by the diffusion of interstitial oxygen atoms towards, and the diffusion of vacancies away from, the inside of the tube wall. A vacancy diffusion mechanism of this type might be expected to result, through time, in the formation of stable voids produced by aggregation of vacancies. These voids will act as a low energy sink for further vacancies and will, therefore, grow producing micro-porosity and as the process continues pin-holes will be formed. Oxygen can then pass into the tube by Knudsen flow. The suggested mechanism therefore accounts for the initial permeation of oxygen and explains the observed deterioration of the tube material with time.

CHAPTER V

CONCLUSIONS

CONCLUSIONS

The results of this study were extremely disappointing since it proved to be impossible to obtain any values for the activity of carbon in liquid iron. Certain difficulties had been envisaged at the outset of the work. The two major problems appeared to be the development of a technique whereby radioactive carbon in the gases from the reaction chamber could be counted with sufficient accuracy to provide reliable activity values and the possibility that reaction between carbon in the melt and the crucible material would be sufficeintly rapid to interfere with results obtained.

The end-window counting technique first used to measure radioactive carbon dioxide was abandoned since it did not give highly reproducible results and since

it /

it would have required an undesirably high level of radioactivity in the iron - carbon melt. The internal gas counting method subsequently developed, however, was much more satisfactory and is considered to be an extremely accurate and attractive method for the estimation of small quantities of carbonaceous gas.

It had been anticipated that reaction between a metal oxide crucible and carbon in the melt might result in formation of carbon monoxide, leading to errors in the estimation of methane by the radioactive technique. It was shown, however, that in the case of the alumina crucibles used the rate of reaction was extremely low. The fact that some reaction occurred when gas was bubbled through the melt by an immersed alumina tube indicate, however, that quiescent conditions must be /

be maintained at this alumina - metal interface if this source of error is to be avoided.

Although the two initial problems had been satisfactorily resolved, it was found that no further progress could be made due to the formation of relatively large quantities of carbonaceous gas in the reaction chamber. A disadvantage of the radioactive tracer technique in this particular application was that it did not distinguish between methane and carbon monoxide and in order to overcome this the gas chromatography technique was developed. This proved conclusively that carbon monoxide was being formed in the reaction chamber and also indicated that the methane content was below the equilibrium value for a carbon saturated melt.

Having dismissed all possible explanations for the presence /

presence of oxygen in the reaction chamber it was concluded that oxygen was diffusing through the wall of the alumina refractory tube. This conclusion, although in excellent agreement with the experimental evidence, was very surprising since there was no reports of such a mechanism in the literature. It has, however, been subsequently supported by Hayes et al [33]. This difficulty makes the present study virtually impossible since even the best tubes, which show only very little diffusion of oxygen at the outset quickly deteriorate at high temperature in the presence of hydrogen.

The conclusion that alumina refractory tubes become permeable to oxygen at high temperatures is extremely important, since many experiments can be envisaged where a low partial pressure of oxygen is required. It is now quite /

quite clear that such an experiment would be impossible if the technique involved heating the alumina tube to a high temperature.

It is doubtful whether the use of a different refractory tube material would improve the results. Mullite was shown in the present investigation to have, if anything, worse properties and the only other alternative would appear to be stabilised zirconia, which might be expected to allow oxygen diffusion by a similar mechanism. It has in fact been learnt [34] that permeation of oxygen through zirconia has been observed.

The only way in which this problem could be overcome would be by the use of a technique in which the wall of the reaction chamber is kept cool. This could be achieved by the use of inductive heating. However, such /

such a technique would have required extensive alterations to the experimental apparatus and since the diffusion of oxygen was confirmed only in the latter stages of this study there was unfortunately insufficient time to investigate the possibilities of alternative heating methods.

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